Fundamental Investigation of Fuel Transformations in Pulverized Coal Combustion and Gasification Technologies

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ABSTRACT

The goal of this project was to carry out the necessary experiments and analyses to extend current capabilities for modeling fuel transformations to the new conditions anticipated in next-generation coal-based, fuel-flexible combustion and gasification processes. This multi-organization, multi-investigator project has produced data, correlations, and submodels that extend present capabilities in pressure, temperature, and fuel type. The combined experimental and theoretical/computational results are documented in detail in Chapters 1-8 of this report, with Chapter 9 serving as a brief summary of the main conclusions. Chapters 1-3 deal with the effect of elevated pressure on devolatilization, char formation, and char properties. Chapters 4 and 5 deal with advanced combustion kinetic models needed to cover the extended ranges of pressure and temperature expected in next-generation furnaces. Chapter 6 deals with the extension of kinetic data to a variety of alternative solid fuels. Chapter 7 focuses on the kinetics of gasification (rather than combustion) at elevated pressure. Finally, Chapter 8 describes the integration, testing, and use of new fuel transformation submodels into a comprehensive CFD framework. Overall, the effects of elevated pressure, temperature, heating rate, and alternative fuel use are all complex and much more work could be further undertaken in this area. Nevertheless, the current project with its new data, correlations, and computer models provides a much improved basis for model-based design of next generation systems operating under these new conditions.

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EXECUTIVE SUMMARY

The goal of this project was to carry out the necessary experiments and analyses to extend current capabilities for modeling fuel transformations to the new conditions anticipated in next-generation coal-based, fuel-flexible combustion and gasification processes. This multi-organization, multi-investigator project has produced data, correlations, and submodels that extend present capabilities in pressure, temperature, and fuel type. The main issue for pyrolysis is the effect of pressure for coals of various rank. By generating chars in both atmospheric and pressurized flat-flame burners (up to 15 atm), the team found a number of important trends. Chapters 1 and presents experimental data needed to extend coal pyrolysis models to high pressure, including effects on volatiles yield, swelling, H/C and O/C ratio, surface area, and char reactivity. Important differences are seen as a function of pressure, and the combined data allow these differences to be accounted for in CFD models. Chapter 3 describes high-pressure, high-temperature char combustion experiments and their analysis with a combination of Fluent and the CPD and CBK submodels. A different value of the char combustion reactivity (activation energy or pre-exponential factor) for each pressure condition for each coal, highlighting the importance of pressure effects that must be accounted for in advance combustor / gasifier design.

Chapters 4 and 5 present new results on char combustion kinetics and their extension to wide ranges of pressure and temperature. A major result is the first theoretical justification for the long-standing paradox of persistent, high fractional order in the char/oxygen reaction is surface heterogeneity. This work provides sufficient underpinning to justify the use of the power-law form in practical char combustion modeling. The use of the power-law form has practical advantages, but to date has lacked a fundamental basis and has led to much controversy and confusion in the field.

There continues to be interest in the development and applications of more detailed rate expressions. If the field proceeds in that direction, this work suggests that the common 2-step Langmuir form is unsuitable, as it cannot predict the high fractional orders almost universally seen at low temperature. A possible promising direction is the use of three-step or four-step semi-global mechanisms incorporating O₂-complex reaction as described here in Chapter 4. It remains to be seen if the added complexity relative to power-law approaches will make this a popular approach in design applications. The heterogeneous surface model of Haynes is also shown to be a promising framework for describing the major features in the char combustion database though it requires a statistical treatment of active sites.

Chapter 6 describes experimental work addressing the issue of fuel flexibility anticipated in next generation systems by providing a large database of comparative reactivities on coals and alternative solid fuels. A hybrid chemical/statistical model was developed that explains most of the observed reactivity variation based on four variables: the amounts of nano-dispersed potassium, nano-dispersed calcium and magnesium, elemental carbon wt-%, and nano-dispersed vanadium, listed in decreasing order of importance.

Chapter 7 deals with *gasification* mechanisms at elevated pressure. CO₂ gasification reactivities were determined for two char and the effects of total CO₂ pressure, CO₂ partial pressure, and the inhibition effect of CO on the reaction rate were investigated at elevated pressures. The results show that char reactivity increases monotonically with CO₂ partial pressure and the apparent activation energy *decreases* with *increasing* pressure. Further, reactivity *decreases* considerably with increasing CO partial pressure. Finally Chapter 8 describes a task in which advanced coal combustion submodels, Chemical Percolation and Devolatilization (CPD) and Carbon Burnout Kinetic (CBK) were modified and incorporated into a comprehensive computational CFD code.

Overall, the effects of elevated pressure, temperature, heating rate, and alternative fuel use are all complex and much more work could be further undertaken in this area. Nevertheless, the current project with its new data, correlations, and computer models provides a much improved basis for model-based design of next generation systems operating under these new conditions.

PROJECT BACKGROUND

Increased concern over energy supply and global warming is currently motivating a major research effort in the U.S. on future energy technologies with low CO₂ emissions. Research is needed to configure and design future coal-fired power-generation technologies with no or minimum impact on atmospheric CO₂ concentrations. A reduction in CO₂ emissions can be accomplished in the near term through increased efficiency with existing systems. Integrated gasification combined cycle (IGCC) systems have been used as the starting point for strategies to reduce CO₂ in the atmosphere, since (a) they are more efficient than conventional systems (50-60% as opposed to the current 34%) and (b) they promise to provide a concentrated stream of CO₂ by using steam and pure O₂ as the gasification agents (without N₂ as a diluent). Sequestration processes are currently under development that rely on IGCC, but this technology has not yet been widely demonstrated. In addition to IGCC, systems, combustion systems operating with enhanced oxygen concentration or pressure may also provide concentrated CO₂ streams.

Role of Model-Based Design

Within the last several years computational fluid dynamics (CFD) has firmly established itself as an important tool for the design, optimization, and retrofit analysis of full-scale combustion furnaces. CFD tools, when expertly applied, can identify firing configurations that significantly enhance performance and avoid the need for full-scale testing. Computer simulation is even more important for the design and development of next generation energy technologies based on oxygen-enriched combustion and/or gasification. These advanced systems cannot be reliably designed in an evolutionary way, as is often the case with current technologies, since there is no extensive database of operating experience with similar units. Model based design requires fuel-general submodels of coal transformations that are accurate under the combustion and gasification conditions unique to these processes.

Fuel Transformation Submodels

Successful furnace simulation requires predictive capabilities for many subprocesses including fuel transformation submodels to predict: (1) pyrolysis and char yield, (2) char oxidation and carbon burnout, (3) nitrogen release, and (3) mineral transformations. One of the P.I.s, (T. Fletcher) is the primary architect of the chemical percolation devolatilization (CPD) model (Fletcher et al. 1992), a mechanistic pyrolysis model based on a network description of the chemical structure of the parent coal. The model: (a) is suitable for application in large comprehensive models of coal combustion, and (b)

accurately describes key chemical structural features and reaction mechanisms of coal. Another of the Principal Investigators (R. Hurt) been engaged over the last eight years at the Combustion Research Facility at Sandia National Laboratories and at Brown University in the development of advanced submodels for char combustion, with emphasis on carbon burnout prediction. Carbon burnout has become a critical issue in the existing boiler stock as low-NO_x burner retrofits have increased carbon carryover and seriously impacted ash utilization markets at many sites in the U.S.. The experimental work has led to the Carbon Burnout Kinetic Model (CBK), a fuel-general kinetics package designed to predict carbon burnout under conditions relevant to current pulverized coal-fired boilers [Hurt et al., 1998]. Special emphasis is given to the late stages of combustion, which exert a strong influence on the burnout process that determines the carbon content of ash and thus ash utilization options [Hurt, 1998].

The fuel submodels listed above have been developed and applied for atmospheric pc-fired combustion systems. In this application they have found practical use in industry codes and have demonstrated some predictive capability, but further validation against field data is needed, as is extension to conditions found in next-generation energy processes. Although many of the condensed phase processes (internal diffusion, thermal annealing) can be directly carried over into models of gasification and O₂-enriched combustion, other reaction processes in the condensed phases require new data to make predictions under these conditions. Specifically new data is needed on: (1) the char formation process at high pressure, (2) char surface kinetics in enhanced oxygen and in the complex gasification environments, (3) nitrogen and inorganic release at high pressure and the concomitant high particle temperatures of enhanced oxygen combustion and oxygen-blown gasification systems, and (4) the development of engineering models that combine char property prediction with simplified surface kinetics for inclusion in practical flame codes.

PROJECT OBJECTIVE AND APPROACH

To carry out the necessary experiments and analyses to extend leading submodels of coal transformations to the new conditions anticipated in next-generation energy technologies. The work will use a combination of high-pressure TGA, atmospheric entrained flow reactor experiments, and experiments with a high pressure drop tube furnace to address volatile release, nitrogen release, inorganic release, and char properties and reactivity,

with particular emphasis on gasification environments under pressure and enhanced oxygen environments at atmospheric pressure. The CPD and CBK models will be validated against full-scale data on current pc-technologies with industry involvement (McDermott / B&W) and will be extended to the new conditions using the data generated in the experimental portion of the program.

To achieve the above project objective, a multi-university / joint industry team has been assembled, consisting of Brown University (P.I.s Robert Hurt and Joseph Calo), Brigham Young University (P.I. Thomas Fletcher), and McDermott's Babcock and Wilcox Power Generation Group (P.I. Alan Sayre). The research work will be divided into the following four tasks, with the leading participants identified:

- Task 1: Char Formation and Inorganic
(Fletcher, BYU)
- Task 2: Combustion Kinetics
(R. Hurt, Brown)
- Task 3: Gasification Kinetics
(Calo, Brown; Fletcher, BYU)
- Task 4: Validation and Extension of CPD and CBK Fuel Submodels
(Sayre, B&W)

The remainder of the report documents the results from this study organized along these task lines. Task 1 is covered in Chapters 1-3, Task 2 in Chapters 4-6; Task 3 in Chapter 7, and Task 4 in Chapter 8. Chapter 9 presents a brief summary statement that highlights the major conclusions and recommendations.

CHAPTER 1 THE EFFECT OF PRESSURE ON COAL PYROLYSIS

1.1 Literature Review

This literature review summarizes previous studies of coal devolatilization and char oxidation with emphasis on issues related to the effects of total gas pressure.

1.1.1 The Effect of Pressure on Coal Devolatilization

Coal pyrolysis at elevated pressure is reviewed here for three categories of reactors: TGA, wire-mesh, and drop-tube reactors.

1.1.1.1 TGA Reactor

The Thermogravimetric Analyzer (TGA) provides the most precise measurements of mass release of reacting material. However, this technique suffers from disadvantages such as low temperatures and low heating rates (<1 K/s). Seebauer and Staudinger (1997) used a TGA to investigate the effects of pressure, particle size, and heating rate on coal pyrolysis. They indicated that the total volatile yield decreased with increasing pressure, with a significant decrease in tar yield and a slight increase in light gas yield with increasing pressure. The TGA experiment alone is insufficient to derive kinetics parameters for pyrolysis reactions due to (a) the low heating rate, and (b) large effects from the bed of particles. Sun et al. (1997) studied the pyrolysis of two Chinese coals (0.4-4 mm) under pressure (1-13 atm) using a pressurized dual-chamber TGA with a heating rate as low as 0.33 K/s. Their results showed that the total volatile yield decreased with increasing pressure, while the total mass release was almost independent of pressure at low temperature (< 873 K). Arendt and van Heek (1981) performed high-pressure pyrolysis for five German coals using a wire mesh reactor and TGA respectively, and found similar trends with respect to pressure.

1.1.1.2 Wire-Mesh Reactor

The electrical grid or wire mesh reactor has been widely applied to coal pyrolysis due to the heating rate of the facility being well controlled. Anthony and Howard (1976) and Suuberg et al. (1978) showed that increasing pressure from 10^{-4} to 69 atm in 1000K/s experiments with 30 s hold reduced total volatile yield by roughly 5 wt% for lignite and

15 wt% for bituminous coal. Arendt and van Heek (1981) found that with increasing pressure, tar repolymerised and cracked more significantly, resulting in increased yields of char and hydrocarbon gases. Hydrogen was found to influence devolatilization significantly at increased pressures. Additional amounts of aromatic products were released by hydrogenation of coal itself, particularly between 773 and 973 K, and the yields of light products such as CH_4 and C_2H_6 increased significantly.

Griffin et al. (1994) studied the effects of pressure (1-10 atm) and temperature (750-1230 K) on pyrolysis of pulverized Pittsburgh No. 8 bituminous coal under a helium atmosphere, using an electrical screen heater reactor at a heating rate 10^3 K/s. They found that volatile yields decreased slightly with increasing pressure, the effect being more pronounced at higher temperature. Below 970 K, pressure had little effect on yields. This is similar to the results obtained by Anthony and Howard (1976) and Bautista et al. (1986), who studied high pressure pyrolysis for four different coals using an electric grid reactor at heating rates from 100-10,000 K/s. They found that the weight loss of Pittsburgh coal decreased rapidly with increasing pressures of helium and hydrogen to an apparent limiting value at 10 atm. The decrease in weight loss with increasing pressure was attributed to diminishing tar yields, only slightly compensated by increasing gas yields. The tar yields were identical in the inert and reducing atmospheres, so consistently higher gaseous yields under hydrogen resulted in the increased mass release. Cai et al. (1996) studied coal pyrolysis with a hydrogen pressure up to 70 atm in a wire-mesh pyrolysis reactor at heating rate 1 to 5000 K/s. They observed an increase of total volatile yield with increasing H_2 pressure, while tar yields decreased and the degree of reduction in tar yields decreased with increasing pressure. Cai's results showed that the influence of pressure on volatiles yields and tar yields became more significant at higher temperatures.

1.1.1.3 Drop-Tube Reactor

Lee et al. (1991) investigated the rapid pyrolysis behavior of a bituminous coal under rapid heating (10^3 - 10^4 K/s) and elevated pressure (up to 3.8 atm) relevant to gasification. They found that increasing pressure slowed the global release of volatiles, lowered the asymptotic volatile yields, and promoted secondary reactions of the volatiles, which

reduced the tar yields and changed the gas yields. Fatemi (1987) investigated the effect of pressure on devolatilization of pulverized coal particles up to a temperature of 1373 K and pressures of 68 atm in an entrained flow reactor. The results showed that tar yield is affected by pressure, decreasing significantly with increasing pressure up to 13.8 atm. Weight loss and gas yield decreased with increasing pressure up to 13.8 atm, but at higher pressures there was no significant effect. Yeasmin et al. (1999) studied the high-pressure devolatilization of brown coal using a pressurized drop tube furnace. The residence time of coal particles in the furnace was calibrated based on the effect of pressure and temperature. Partially devolatilized coal or char particles were collected using a collection tube, which was able to move up and down to control the residence time in the furnace. Weight loss decreased with increasing pyrolysis pressure. In a recent study, Matsuoka et al. (2003) examined three Japanese coals using a drop tube reactor, with temperature ranging from 600 to 700°C. The effect of pressure was significant on CH₄ and C₂-C₆ hydrocarbon fractions. The yields of CH₄ and CO₂ increased with increasing pressure, whereas C₂-C₆ yields monotonically decreased with increasing pressure.

1.1.1.4 Summary

In summary, the effects of pressure on devolatilization behavior vary with coal rank, gas environment and operating conditions. General trends observed from experiments can be summarized as follows:

The total volatile and tar yields decrease with increasing pressure, tar yield being more distinctly dependent on pressure. The reduction in tar and total volatile yields appears to be most significant for bituminous coals, but less pronounced for lignite. The effect of pressure on tar and total volatile yields appears to be more pronounced at higher temperature. The effect of pressure on the tar and total volatile yields appears to be less pronounced at high pressure. With increasing pressure, tar molecular weights are lower.

Although the effect of pressure on coal pyrolysis has been extensively researched, entrained flow high pressure coal pyrolysis research is still needed. TGA pyrolysis tests

are limited by low temperature and low heating rate. Wire-mesh reactors have the drawback of interaction between coal particles and the wire mesh. Many current drop tube reactors can not achieve high temperatures ($>1200^{\circ}\text{C}$) at high pressure, and the particle heating rate typically only reach 10^4 K/s compared to 10^6 K/s in industrial facilities. A high-pressure flat flame burner was therefore developed in this study to overcome these problems.

1.1.2 Effect of Pressure on Resulting Char Physical Properties

Coal devolatilization affects the combustion performance of pulverized fuel boilers in many different ways. The primary influences of coal devolatilization on char combustion are (a) the amount of mass released as volatile matter, and (b) the heating value of pyrolysis product, which have been discussed in section 1.1.1. An equally important aspect is mass remaining in the char. The physical structure of char subsequent to devolatilization (i.e. diameter, internal surface area, pore size, and porosity) determines the rate of char oxidation. This section focuses on the effects of coal devolatilization at elevated pressure on the physical structure of the char products. Coal swelling, morphology, surface area, and pore size will be discussed.

1.1.2.1 Coal swelling ratio during devolatilization

The swelling ratio may be the most distinct phenomenon of coal physical structure transformation during devolatilization, which can affect char particle size, pore size, porosity, density, and reactivity. The swelling ratio can be affected by coal properties such as particle size, coal rank, maximum temperature, heating rate, and oxygen content. This issue becomes more complicated when considering the diversity of the behavior of individual particles during heating due to the variation of the coal maceral constituents among the particles within the same coal sample (Benfell et al., 2000). Instead of a comprehensive review of coal swelling research, this section only focuses on pulverized coal swelling at elevated pressure.

Direct observations (Essenhig and Yorke, 1965; Gao et al., 1997; Strezov et al., 2003) of coal swelling at low heating rates were relatively easy compared to harsh industrial flame conditions. It was observed that coal particles undergo significant changes of

swelling and shrinking, followed by a rapid contraction repeating until resolidification occurred. Fletcher (1993), Gale et al. (1995), and Zygourakis (1993) observed the transient swelling of fuel particles in situ at high heating rates during pyrolysis at 1 atm. The general trend of coal particle swelling ratio with heating rate is shown in Figure 1.1. Coal particle swelling ratio increases with increasing heating rate to $10^3 \sim 10^4$ K/s, and then decreases at higher heating rate.

Figure 1.1. Swelling vs. heating rate at 1 atm (Gale et al., 1995).

Lee et al. (1991) studied the effect of pressure on the swelling behavior of Illinois #6 coal pyrolyzed at 1189 K in an inert Nitrogen atmosphere. At 1 atm, coal particle swelling was not significant. At 8 atm, swelling based on diameter increased about three times at 0.3 s and thirty times at 0.8 s, suggesting swelling may occur during later stage of pyrolysis. However, at 22 atm, the extent of swelling dropped significantly, and swelling occurred in the early stage of pyrolysis, where significant mass release occurred. Wu et al. (2000) studied an Australian bituminous coal using a pressurized drop tube furnace. The char characteristics were found to be influenced significantly by the system pressure.

Results obtained indicated that the coal and char fragmentation might have occurred during devolatilization at high pressure. The char size (as characterized by the swelling ratio) was also observed to increase with system pressure. The measured swelling ratios of the char sample fall well below the data by Lee et al. (1991) at all system pressures. This may be caused by differing furnace temperatures or heating rates, which are compared in Table 1.1. Yu et al. (2003) studied the effect of initial coal density fractions on their swelling ratio. The mass release, swelling ratio, and the porosity decrease with increasing parent coal density. Results of size fraction samples suggest that a larger swelling occurs in DTF (drop-tube furnace) when the particle size decreases.

Table 1.1 Comparison of Experimental Conditions for 2 Pressurized Drop Tube Experiments

	Lee et al.(1991)	Wu et al. (2000)
Coal	Illinois No.6	Australian Bituminous coal
Particle size	62 μ m mean particle diameter	63-90 μ m
Apparatus	HEF (high-pressure entrained-flow furnace)	PDTF (pressurized drop-tube furnace)
Heating rate	$\sim 10^4$ K/s	$\sim 10^4$ - 10^5 K/s
Temperature	1189 K	1573 K
Pressure	0.1-3.8 MPa	0.1-1.5 MPa
Atmosphere	N ₂	N ₂ with small amounts of O ₂

A number of attempts have been made to model the coal swelling (Oh et al., 1989; Sheng and Azevedo, ; Solomon and Hamblen, 1985; Yu et al., 2002). It is commonly agreed that metaplast fluidity and bubbles formed during coal devolatilization play an important role on determining coal swelling ratio and char structure. The fluidity of the metaplast of the softening coal can be improved by increased pressure, due to the retention of volatiles which act as a plasticizing agent (Khan and Jenkins, 1984). The increased fluidity facilitates bubble transport to the particle surface. Elevated pressure also increases the resistance to expansion of the plastic coal melt (Lee et al., 1991). The maximum swelling ratio occurs at the point that initial pressure build-up inside coal melt achieves a balance with bulk pressure. When the bulk pressure is higher than the inflection point, bubble

contraction can be observed. Bubble growth and coalescence can also be used to explain char physical structure change with density (Yu et al., 2002).

1.1.2.2 Coal morphology and surface area during devolatilization

Char morphology has been extensively studied during past decade (Alvarez et al., 1997; Cloke et al., 1997; Lester and Cloke, 1999; Lester et al., 1996). Recently, Wu et al. (2000) and Benfell et al. (2000) studied the effect of pressure on char morphology. By analyzing char SEM (Scanning Electron Microscopy), chars were categorized based on criteria shown in Table 1.2.

Typically, Group I particles have a very porous structure, with large voids inside the particle and a thin wall, Group II particles have a medium porosity and wall thickness, while Group III char particles have low porosity. This classification is the first such attempt. Effects of coal rank and density on coal morphology were also studied by Bailey et al. (1990) and Benfell et al. (2000). Essentially, coal rank and density are indexes of coal petrography. The morphology of the chars shows a strong relationship with increasing vitrinite content (Benfell et al., 2000).

Table 1.2 Char Classification System (Benfell et al., 2000; Wu et al., 2000)

Char groups	Group I	Group II	Group III
Two-dimensional schematic representation
Porosity (%)	>70	Variable, 40–70	<50
Average wall thickness (mm)	<5	>5	>5
Shape	Spherical subspherical	Subspherical	Angular
Typical swelling ratio	>1.3	<1.0	<0.9
Typical residual mass ratio	0.1–0.5	0.1–0.5	1.0

Pressure has a strong influence on coal morphology. When furnace pressure increases, the overall proportion of Group I chars formed increases, while the proportions of Groups II and III chars decrease. Mean diameter and sphericity of coal A increased with pressure.

Mean diameter and porosity of coal CV increased at pressure between 5 and 10 atm, then decrease from 10 to 15 atm, probably due to char fragmentation. Microscopic observation of this char showed that the group I particles had thinner walls and a more spherical structure than those of lower pressure chars, factors which made this sample more susceptible to fragmentation within the furnace and during handling (Benfell et al., 2000). Compared to the low-pressure char, the average macro-porosity of high-pressure chars was higher, and they had larger number of bubbles with smaller sizes (Yu et al., 2003).

The internal surface area of char is one of the significant parameters used for char combustion and gasification modeling. Only two data sets have been presented for the surface area of chars produced under high-pressure conditions. Lee et al. (1991) investigated the development of CO₂ surface area of char as a function of mass release and pressure for Illinois No. 6 bituminous coal under a low heating rate condition (Table 1.1). The surface area of char is generally lower under higher pressure pyrolysis conditions. The development of surface area is relevant to the thermal-plastic property of coal during heating. A recent study presented the CO₂ surface area for chars produced from Australian bituminous coals in a pressurized drop tube furnace at various pressures (Benfell et al., 2000). Generally, the surface areas of chars decreased as pressure is increased. The effect of pressure on char surface area is believed to be related to the fluid behavior during devolatilization (Lee et al., 1991).

1.2 Objectives

The objective of this part of the project is to study the effects of pressure on coal pyrolysis at high heating rate, typical of practical pulverized coal combustion. High-temperature, high-pressure pyrolysis experiments were conducted on four bituminous coals. The resulting chars were collected and analyzed to find the effect of pressure on the coal pyrolysis process and the char structure properties. This chapter focuses on the following aspects: mass release during pyrolysis processes, char elemental composition, char swelling ratio, char physical structure, and char surface area.

1.3 High-Pressure Facility at BYU

The conditions required for high temperature, high pressure coal pyrolysis and oxidation experiments place strict demands on the test facility, especially when simulating industrial-scale pulverized coal combustion conditions. Basically, the following conditions need to be met for a realistic experiment:

1. High particle heating rates ($10^4 \sim 10^6$ K/s);
2. High gas temperature for coal pyrolysis and high particle temperature (1700~2200 K) for char combustion;
3. Stable temperature zone for coal particles to react during the oxidation process;
4. Reaction residence times and gas compositions for particle oxidation must be stable and adjustable;
5. Single particle reaction behavior.

The difficulties associated with implementing these requirements are reasons that there is a lack of reliable high temperature, high pressure coal combustion data.

1.3.1 Review of Char Oxidation Facilities

Coal pyrolysis and char oxidation experiments have been conducted for over several decades, and have mainly been studied in heated grids and thermogravimetric analyzers (TGAs). Some coal pyrolysis and char combustion experiments are also performed with flat flame burners, or shock tubes. The previous section evaluated the advantages and disadvantages of drop-tube furnaces, heated grids, and TGAs. Flat flame burners (FFBs) were used widely in atmosphere coal combustion studies (Fletcher, 1993; Mitchell, 2003), since they can closely approximate pulverized fuel combustor conditions, have high heating rates and high gas temperatures, and are easy to start up. On the other hand, flat flame burners use methane or carbon monoxide as fuel, limiting the gas compositions of combustion products (e.g., there are significant concentrations of steam for methane flame). Isothermal temperature profiles in FFBs are also difficult to maintain.

Shock tubes can be operated at elevated pressure without being too expensive, but several drawbacks limit their usefulness: (1) The short reaction time (several milliseconds) result in very unsteady particle temperature histories (Lester et al., 1981); (2) particles cannot be sampled in various stages of burnout; (3) the range of gas concentrations is limited; and (4) particle dispersion and agglomeration have proven to be problematic (Essenhigh, 1981).

Although one apparatus may be better than others in one or several aspects, certain prerequisites need to be satisfied to achieve a reasonable simulation of pulverized coal combustion. For the elevated pressure coal combustion study, basic prerequisites are (Niksa et al., 2003):

1. Pressure: a uniform pressure should be maintained through reaction process.
2. Thermal history: Sufficient information must be available to assign the temperature of the samples as a function of time throughout an entire process. High heating rate ($>10^5$ K/s) is needed at coal/char initial heating stage, and high gas temperature (>1400 K) is needed for char combustion experiments.
3. O_2 partial pressure: Uniform O_2 levels in the free stream throughout a combustion history can only be imposed with very dilute coal suspensions. O_2 partial pressure can be controlled.

These prerequisites may be closely approximated by a drop-tube furnace. A drop-tube furnace consists of a long, vertical reaction tube through which passes a laminar flow of gas. Two gas flows are introduced at the reactor entrance. The primary flow is introduced at the center of the reaction tube through an injection probe. The secondary flow, preheated to a certain temperature, enters the reaction zone through the annulus between the reaction tube and the injection tube. Carried by the primary flow, the small stream of particles enters the reaction zone, and flow along the reaction tube axis, reacting with the surrounding gases. These reactions are quenched as the particles enter the cooled collection probe, located at the reactor exit. The injection tube or the collection probe is moveable to allow various particle residence time. Electric wall heaters are normally used

to provide heat to the reaction tube, and the preheating is achieved by plasma, a combusting flame, or electric heaters.

Drop-tube furnaces have been widely used in high-pressure coal pyrolysis and char combustion studies (Lee et al., 1991; Monson, 1992; Reichelt et al., 1998; Wu et al., 2000). There are several drawbacks related to drop-tube furnaces. The heating rate of particle in drop tube furnace can only be as high as 10^4 K/s, caused by the slow heat transfer rate from the secondary flow to coal particle. It has also been observed that insulating characteristics of the refractory degraded sharply with increasing pressure (Monson, 1992), which make it very difficult to achieve a high temperatures. One possible solution to this dilemma is to introduce a flat flame burner in drop tube furnace. This attempt was implemented in the current project and will be described in the following sections.

1.3.3 BYU HPDT Reactor

A high pressure drop tube (HPDT) reactor was previously designed and constructed for use in both devolatilization and char oxidation tests (Monson, 1992). This drop tube reactor was later upgraded by changing from molybdenum disilicide heating elements to an Iron-Chrome-Aluminum ceramic-coated high temperature heater, which had greater longevity than the original heating elements (Hambly, 1998).

Figures 1.2 and 1.3 show schematics of the high pressure drop tube reactor. The drop tube reactor (Figure 1.2) is an electrically-heated laminar flow drop tube which was operated at pressures as high as 15 atmospheres (Monson, 1992). Maximum particle heating rates were about 10^4 K/s. Separate cylindrical electrical resistance heaters were used in the preheater and drop tube sections, each with separate set points and control thermocouples. Each control thermocouple was kept at a constant operating temperature by a PID controller. The pre-heater section heated the (secondary) nitrogen stream to about 625 K before it entered the drop tube. A water-cooled injection probe entrained the coal particles in a small (primary) nitrogen flow and prevented the particles from being heated until they left the probe. The residence time was changed by either raising or

lowering the injection probe, or by changing the gas flow rate. The particles were injected at a slow rate ($\sim 1\text{g/hr}$) in order to approximate single particle behavior. The secondary (pre-heated) and primary (injection probe) nitrogen flows were set so as to attempt to match their radially-averaged gas velocities (about 0.7-0.85

Figure 1.2. Schematic of High Pressure Drop Tube Reactor (Hambly, 1998).

m/s). In this way it was hoped to minimize turbulence at the point of injection so that the particles would flow down the center axis of the drop tube with minimal dispersion. The direct observation of particle flow near the reaction tube exit showed that particles flowed along the centerline.

Figure 1.3. Schematic of drop tube reactor sample collection configuration(Perry, 1999).

Gas temperatures along this center axis were carefully measured with the injection and collection systems in place (except for the cyclone) using a type S thermocouple inserted from beneath the virtual impactor. Measured gas temperatures were corrected for radiative losses from the thermocouple bead. Pyrolysis products in the drop tube were immediately quenched by dilution with cool (300 K) nitrogen gas upon entering a water-cooled collection probe. Char was separated from most of the tar by a virtual impactor followed by a one-inch cyclone (Perry, 1999).

The HPDT could not achieve high temperatures at elevated pressures. Figure 1.4 shows the centerline temperature profiles of HPDT at different total pressure and a fixed gas flow rate. By adjusting the set point of the heaters, the temperature profiles were maintained at 1200 K. At 15 atm total pressure, the set point of preheater had to be lowered down to 580°C to avoid failure of the controller unit. Most hear loss was observed at elevated pressure, since denser gas promoted heat loss through the insulation on the reactor wall.

Figure 1.4. Measured gas temperature profiles in the HPDT.

A series of devolatilization tests of Pitt #8 coal were conducted on HPDT at 1, 6, and 11 atm total pressures. The hydrogen contents of the chars collected were around 2 wt%, which is much higher than the hydrogen content (0.5%) of char normally collected from an atmospheric flat flame burner. Since it was not possible to obtain fully pyrolyzed chars in the HPDT at elevated pressures, due to heat loss limitations, it was necessary to develop another system.

1.3.3 High Pressure Flat-Flame Burner (HPFFB) Reaction System

The high-pressure flat flame burner developed in this project was designed based on an atmospheric pressure FFB used by Ma (1996). The atmosphere FFB was also used for some comparison tests in this project. A schematic of the HPFFB is shown in the Figure 1.5.

The high-pressure flat flame burner uses the hot products of methane combustion to heat the particles. As shown in Figure 1.5, methane flows through hypodermic tubes and combusts with oxidizer, which is either air or a mixture of air/O₂. The “flat-flame” therefore consists of an array of small diffusion flamelet located about 1 mm from the burner surface. The combustion in these flamelets is completed quickly (flame thicknesses at 0.5 to 1 mm), providing an uniform post-flame environment. Post-flame gas temperature and composition can be adjusted by changing the equivalence ratio or oxidizer composition. Residence time can be changed by raising or lowering the burner relative to the collection probe. Coal particles were injected along the center axis of a 2 inch diameter quartz tube. In order to approximate single particle behavior (i.e. no particle-particle interactions), the coal particles were fed at a rate of less than 1 g/hr by entrainment in a small stream of nitrogen. Maximum particle heating rates in the flat flame reactor were about 10⁵ K/s.

Figure 1.6 is a flow diagram of the HPFFB facility. High pressure nitrogen, air, oxygen, and methane were provided by a reservoir of high pressure gas bottles, with pressure regulators set to 400 psig. Four Porter flow controllers were used to control the flow rates of primary gas (N₂), methane, air, and oxygen. Nitrogen flow used to pressurize the system was monitored by a flow meter, and the flow rate was manually adjusted. Nitrogen quench flow was also controlled in the same manner. Air and oxygen were premixed during char oxidation experiments to increase oxygen concentration. The O₂ concentration in the reactor exit stream was monitored with an O₂ sensor before each coal experiment. An Omega PID controller read the reactor pressure from a pressure transducer, and then controlled the system pressure by adjusting orifice size of a valve located in the reactor exhaust line (after the particle collection system). An electronic

heater was used to decrease the heat loss from the reactor walls at elevated pressure. Platinum-rhodium thermocouples were installed along the length of reaction tube to monitor gas temperature, and a PID controller was used to control the temperature of the heater.

Figure 1.5. Schematic of the HPFFB.

Figure 1.6 Schematic of the High Pressure Flat Flame Burner flow system.

1.4 Coal Pyrolysis and Resulting Char Properties

1.4.1 Coal Characterization

The main body of pyrolysis experiments was conducted on the four coals listed in Table 1.3, ranging from lignite to high-volatile bituminous coal. The size of coal particles used ranged from 45 to 130 μm . Typical particles used in pulverized coal furnace applications have a mean diameter of $\sim 50 \mu\text{m}$. Oxygen content was determined by difference.

Because the sulfur values as determined by the elemental analyzer include both organic and inorganic sulfur, the oxygen values are somewhat underestimated.

Table 1.3 Characteristic of Coals

Coal	Rank	d (μm)	Proximate Analysis (Wt %)			Ultimate Analysis (wt%, daf)				
			Moisture	Ash (dry)	VM (daf)	C	H	N	S	O ^a
Pitt #8	HvA-Bit	63-90	1.44	10.7	34.34	84.58	5.47	2.00	0.49	7.44
Ken #9	HvB-Bit	44-74	8.21	8.43	42.11	76.72	5.27	1.81	3.72	12.4
Ill #6	HvC-Bit	74-90	3.31	9.35	53.83	78.02	5.45	1.36	4.14	10.5
Knife River	Lignite	45-75	11.91	20.3	47.86	62.23	4.23	0.95	1.28	31.3

a. $O = 100 - (C + H + N + S)$

1.4.2 Reaction Conditions for the Pyrolysis Experiments

All of the elevated pressure chars preparation experiments were conducted using the methane-air high-pressure flat flame burner (HPFFB). Maximum gas temperatures were 1300°C at pressures of 2.5 to 15 atm, with particle heating rates of 10^5 K/s . Atmospheric pressure (0.85 atm) char preparation was conducted using an atmosphere flat flame burner.

In ideal experiments, the pressure could be changed without changing temperature history, residence time, or heating rate. However, this is not possible in an entrained flow

experiment. At high pressure, gas velocity decreases when mass flow rate is held consistent. Gas velocity can be adjusted by increasing the total mass flow rate of entrainment gas, but this changes the heating characteristics (i.e., gas temperature) in the reactor. Residence time is adjusted by changing the reaction length, which was changed by moving the burner up and down. However, excessive heat was lost to the water-cooled burner when the burner was lowered significantly into the furnace.

The high-temperature coal pyrolysis process is usually completed in less than 50 ms, after which little reaction occurs. In this study, all pyrolysis experiments had a residence time longer than 120 ms, and hence collected samples were fully pyrolyzed. The initial plan was to conduct all of the pyrolysis experiments under fuel-rich post-flame conditions, since this worked well in atmospheric FFB experiments. However, the fuel-rich CH₄ flame produced soot at elevated pressures, which contaminated the char samples and affected the experimental results. To avoid this, all of the pyrolysis experiments were conducted in a slightly oxidizing condition (0.2~0.4 mol% O₂) in the post-flame. Such a low concentration of O₂ had a negligible effect on resulting char properties. An O₂ analyzer was used to monitor the composition of the gases exiting the reactor.

The desired flow rates of the combustion gases were determined (a) by computing the adiabatic flame temperatures, and (b) by comparing the measured temperature profiles and O₂ concentrations at different pressures. Table 1.4 lists the flow rates of CH₄ and Air at different pressures.

Table 1.4 Flow Rates Used in the HPFFB

Condition	2.5 atm	6 atm	10 atm	15 atm
CH ₄ (slpm)	1.74	2.16	2.49	2.85
Air (slpm)	17.5	21.5	25	28.5
O ₂ in product (mol%)	0.41	0.32	0.2	0.17
Total flow rate (g/min)	24.295	30.096	34.511	41.732

The centerline gas temperature profile was measured using a type S platinum/rhodium thermocouple inserted from bottom of reactor. The thermocouple bead diameter was 200 μ m. Figure 1.7 shows the measured gas temperature profiles for the four conditions listed in the Table 1.4. Thermocouple readings were corrected for radiation losses. Temperature decreased dramatically at longer distances from the burner as pressure increased. This was caused by larger heat loss at high pressure.

Figure 1.7. Measured gas temperature profile in the HPFFB.

The particle velocity was modeled using Fluent, and the particle velocity profile and gas temperature profile were modeled using the CPDCP code (Fletcher et al., 1990). The effect of primary gas was considered with Fluent modeling. The particle energy conservation equation used in the CPDCP code is:

$$\dot{m}_p c_p \frac{dT}{dz} = h A_p (T_g - T_p) \frac{B}{e^B - 1} - \sigma \epsilon_p A_p (T_p^4 - T_w^4) - \dot{m}_p \frac{dm}{dz} \ddot{A}H \quad (1.1)$$

where $h = Nu k_g / d_p$. In this equation, particle properties are known, and velocity (v_p) was obtained from Fluent modeling results. Gas properties changed with CH_4 /air flow rates,

temperature, and pressure, and were modeled using a chemical equilibrium code. Particle temperature histories calculated at early residence times, characteristic of pyrolysis times, are shown in Figure 1.8 for each pressure. Each condition had a maximum particle heating rate of 10^5 K/s.

Figure 1.8. Calculated early particle temperature histories for the different pressure conditions in the HPFFB. These particular calculations were for the Ill #6 coal.

1.4.3 Mass Release during Coal Pyrolysis Process

The HPFFB coal pyrolysis data were obtained in the 1573 K gas temperature condition at residence times ranging from 231 ms to 2 sec and pressures ranging from 2.5 atm to 15 atm. The atmospheric pressure data (actually 0.85 atm in Utah) were obtained at 1300 K in a separate atmospheric flat-flame burner facility (Zhang and Fletcher, 2001) where the char samples were collected immediately above the luminous devolatilization zone. The total volatiles yield data for the four coals are shown in Figure 1.9 as a function of pressure. The measured volatiles yields exceeded the ASTM total volatiles yields (see Table 1.3) for all coals at low to moderate pressures (< 7 atm); this is apparently caused

by the high pyrolysis temperature, the high heating rate, and the single particle behavior in the HPFFB experiment. The measured volatiles yields of all four coals decreased with increasing pressure. The effect of coal rank on coal mass release is not very clear in this figure, due to the changes in particle temperature profiles and residence times for the different conditions.

Figure 1.9. Measured mass release due to pyrolysis for chars, obtained at different pressures.

The decreased volatiles yield at increased pressure during devolatilization is commonly thought to be caused by two physical processes: vapor-liquid equilibrium effects and transport effects (Fletcher et al., 1990). Bituminous coal tars exhibit a broad molecular weight distribution. As total pressure is increased, tar precursors with high molecular weights no longer have sufficient vapor pressure to evaporate, and are retained in the condensed phase (Solomon and Fletcher, 1994). Elevated pressure also increases the resistance of volatiles leaving the coal particle, possibly decreasing the total volatiles yield (Lee et al., 1991).

The Chemical Percolation Devolatilization (CPD) model (Fletcher et al., 1990; Fletcher, 1989; Grant et al., 1989) was developed to predict devolatilization behavior of rapidly heated coal based on the chemical structure of the parent coal. In this study, coal-dependent input parameters for the CPD model were calculated using proximate and ultimate analysis data using a correlation of previous ^{13}C NMR analyses (Genetti et al., 1999). These input parameters are listed in Table 1.5. Model constants were not tuned to match the volatiles yield data.

Table 1.5 Coal Structure Parameters Used in CPD Modeling

Coal	$M_{\square}$	MW_{cl}	p_0	$\square+1$	c_0
Pitt #8	29.1	344.4	0.5	4.8	0.0
Ken #9	39.2	386.7	0.5	5.2	0.0
Ill #6	40.5	381.4	0.5	5.2	0.0
Knife River	53.3	337.3	0.7	3.7	0.2

In the CPD model, a vapor-liquid equilibrium submodel, based on the molecular weight of tar precursors, accounts for the change in tar yield observed as the total pressure is changed. The CPD model was used to predict the coal mass release using the measured gas temperature profile, the gas velocities predicted using FLUENT software, and the aforementioned particle energy balance (Eq. 1.1). CPD model predictions are shown in Figure 1.10, including predicted tar yields. Each pressure condition was modeled using the appropriate particle temperature history, although lines are drawn through the modeling results for convenience. Modeling results are generally comparable to the experiments for pressures up to 6 atm, and slightly underestimates the measured amount of mass release in this experiment.

1.4.4 Elemental Composition of Chars Prepared at Different Pressures

The elemental compositions of coal chars collected at different pressures are shown in Figure 1.11. For the Kentucky #9 coal, the decrease in H/C ratio between 0.85 and 2.5 atm was due to the difference in temperature between the two experiments (1300 K at 0.85 atm vs. 1573 K at elevated pressures). At higher pressures, the H/C and O/C ratios

increased because less tar escaped from the char due to vapor pressure effects at elevated pressures. Although a decrease in mass release was observed when pressure was increased from 10 atm to 15 atm, both H/C and O/C ratios remained relatively stable when pressure was higher than 6 atm. For the Illinois #6 coal, both H/C and O/C ratios were relatively stable, though the measured mass release decreased slightly with increasing pressure.

Figure 1.10. Predicted and measured mass release as a function of pressure. The solid lines represent predicted volatiles yields using the CPD model, while the dashed lines represent predicted tar yields. (a) Ken #9, (b) Ill #6, (c) Pitt #8, (d) Knife River Lignite.

The stable H/C ratio in the chars at elevated pressure can be explained based on several competing phenomena. First, at increased pressure, the tar yield decreases due to vapor pressure effects in the high molecular weight tar precursors. Thus, the heavier tars are only vaporized at lower pressures. Second, the heavier tars are enriched in carbon and depleted in hydrogen, due to their higher carbon aromaticity than the lighter tars. The tar

that vaporizes at elevated pressure is therefore enriched in hydrogen (Solomon and Fletcher, 1994) beyond the tar evolved at low pressure, but less tar yield is observed at the higher pressure. The tar molecules that would have vaporized at lower pressures, but that stay in the char at elevated pressure, are slightly higher in hydrogen content than the char. These heavier tar precursors that remain in the coal particle serve as light gas precursors, and the evolution of light gas from the char removes hydrogen-rich side chains. Thus, the light gas yield increases as pressure increases, and the light gases are enriched in hydrogen compared to the char. The net effect is that the char H/C ratio remains relatively constant at the elevated pressures.

Figure 1.11. Elemental compositions of chars as a function of pressure. (a) Ken #9, (b) Ill #6, (c) Pitt #8, (d) Knife River Lignite.

Another factor influencing the char H/C ratios in these experiments may be the effect of residence time. The particle residence time in these experiments ranged from 0.3 s to 2.0 s when pressure was increased from 2.5 atm to 15 atm. The total mass flow rate of gas into the reactor increased only slightly with pressure in order to keep the gas temperature

at 1300°C, so as pressure increased, and hence gas density increased, the velocity had to decrease. The ultimate hydrogen content of char can be affected by both the temperature and the reaction time (Genetti et al., 1999). This residence time effect may also offset the higher H/C ratio caused by elevated pressure.

The N/C ratios in the chars do not change significantly as a function of pressure, as shown in Figure 1.11. The fraction of the initial amount of nitrogen that remains in the char can be calculated from the elemental compositions of the coal and char and from the mass remaining (m/m0). Figure 1.12 shows that at least for two of the coals (Ken #9 and Ill #6), more nitrogen remains in the char at increased pressures. The nitrogen release data for the other two coals (Pitt #8 and KRL) are more scattered, but seem to indicate that the fraction of nitrogen remaining in the char stays relatively constant with pressure.

Figure 1.12. Fraction of initial nitrogen remaining in the char ($m_{N,char}/m_{N,coal}$) after pyrolysis as a function of pressure.

1.4.5 The Effect of Pressure on Coal Swelling Ratios

Figure 1.13 shows measured apparent densities as a function of pressure from 1 atm to 15 atm. Fig 1.14 shows the swelling ratios of chars collected at different pressures. The

heating rate of the HPFFB char in this study was estimated to be about 10^5 K/s (see Figure 1.8). This heating rate is higher than the drop tube reactor because there is no wake from the water-cooled coal injector; the particles in a FFB are convectively heated as they pass through a flame front. The experimental conditions of this experiment are compared with other studies (Lee et al., 1991; Wu et al., 2000) in Table 1.6.

Figure 1.13. Apparent densities for chars prepared in the HPFFB.

Figure 1.14. Swelling ratios of four coal chars as a function of preparation pressure.

Table 1.6 Comparisons of Experimental Conditions

	Authors		
	Lee et al.(1991)	Wu et al. (2000)	Current work
Coal	Illinois No.6	Australian Bituminous coal	Two US bituminous coals and one lignite
Particle size	62 μ m mean particle diameter	63-90 μ m	75 μ m average diameter
Apparatus	HEF (high-pressure entrained-flow furnace)	PDTF (pressurized drop-tube furnace)	HPFFB (high-pressure flat flame burner)
Heating rate	$\sim 10^4$ K/s	$\sim 10^4$ - 10^5 K/s	$> 10^5$ K/s
Temperature	1189 K	1573 K	1573 K
Pressure	0.1-3.8 MPa	0.1-1.5 MPa	0.1-1.5 MPa
Atmosphere	N ₂	N ₂ , with O ₂ to burn volatiles	Combustion product of CH ₄ /Air

This high heating rate condition (10^5 K/s) strongly changed the devolatilization characteristics during the early stages of coal pyrolysis, as shown by the comparison of swelling ratios in Figure 1.15. The swelling ratios for coals in the HPFFB were smaller

Figure 1.15. Comparison of swelling ratio in the HPFFB with other studies.

than observed in the PDTF (Wu et al., 2000) or the high-pressure entrained-flow furnace (Lee et al., 1991). Swelling ratios for HPFFB chars still increased with the increase of char preparation pressure. However, the swelling ratios at any pressure for the HPFFB chars are smaller than reported in the experiments with lower heating rates. The swelling ratio of Pitt #8 coal increased when pressure increased, reaching a maximum value at 10 atm, and then dropped at 15 atm. The other coals also exhibited increasing swelling ratios within the pressure range of 1-15 atm, indicating that the effect of pressure on the coal swelling ratio is rank dependent. Similar rank dependent results were reported by Lee et al. (1991).

1.4.6 The Effect of Pressure on Char Morphology

Scanning electron micrographs (SEM) of the chars collected in this study are shown in Figure 1.16. The SEM of cross sections of Pitt #8 and Knife River lignite char samples are shown in Figure 1.17 and Figure 1.18, respectively. The Pitt #8 char particles show evidence of softening bubble formation, and large blow holes where bubbles have ruptured. The 10 atm particles seem to have smaller surface holes than the 6 atm char, which is consistent with the small increase in swelling behavior shown in Figure 1.15. The general features of the lignite chars seem to be void of softening behavior.

Both heating rate and pressure affect swelling characteristics during coal pyrolysis. At low heating rates (such as in a TGA, or ~ 1 K/s), volatiles can diffuse through the pores without causing an internal pressure high enough to cause the particle to swell. At moderate heating rates (such as in a drop tube, or 10^4 K/s), the volatiles formed in the particle interior are formed faster than they can escape through the pores, and swelling occurs if the particle has softened. At high heating rates (approaching 10^5 K/s), the volatiles are formed faster than the swelling process can accommodate, and the bubbles burst. At elevated pressure, higher molecular weight tar precursors do not vaporize, causing more plasticity in softening coals. Hence if conditions are right, enhanced swelling is observed at increased pressures. However, at high heating rates, the surface tension in the bubble walls is overcome and the bubbles burst before significant swelling occurs. For low rank coals and lignites, little softening occurs, and the discharge of moisture and light gases with little tar formation can actually cause particle shrinkage.

The physical structure of the char significantly affects its high temperature oxidation or gasification rate. A comprehensive coal oxidation model needs precise prediction of the swelling ratio. A correlation of coal swelling ratio with pressure and

Figure 1.16. SEM micrograph of char produced from pyrolysis of Pitt #8 coal and Knife River Lignite. (a) Pitt #8 1 atm, (b) KRL 1 atm (c) Pitt #8 6 atm, (d) KRL 6 atm, (e) Pitt #8 10 atm, (f) KRL 10 atm, (g) Pitt #8 15 atm, (h) Pitt #8 15 atm.

Figure 1.17. SEM micrograph of char cross section produced from pyrolysis of Pitt #8 coal (a) 2.5 atm (b) 6 atm (c) 15 atm.

Figure 1.18. SEM micrograph of char cross section produced from pyrolysis of Knife River Lignite (a) 2.5 atm (b) 6 atm (c) 15 atm.

carbon content of the parent coal was developed by Benfell (2001), which predicts change of the coal swelling ratio with increased pressure from medium heating rate coal pyrolysis ($\sim 10^4$ K/s), but overestimates swelling ratio for high heating rate pyrolysis ($\sim 10^5$ K/s). Since practical pulverized coal combustion occurs at high temperature (2000K) and heating rate (10^6 K/s), such correlations should include the effects of heating rate.

SEM images of the external surface of the Kentucky #9 chars produced at pressures of 0.85, 2.5, 6, 10, and 15 atm are shown in Figure 1.19. The letters a-e in the top left corner of each image represents increased pressure condition, respectively. The exterior morphology of char particles clearly changed with increasing pressure. The surfaces of chars produced at 0.85 and 2.5 atm show similar characteristics. The particles have a porous external surface, with blow holes created by volatiles as the internal particle pressure overcame the surface tension of the softened particle. Some smaller char fragments were also observed, possibly caused by fragmentation at these high heating rates. The char particle surface became less coarse as pressure increased from 6 atm to 15 atm, and bubbles were clearly visible beneath the particle surface, which implies a thin wall. Only a small number of fragments were visible at the elevated pressures, and blow holes were not observed like in the char produced at lower pressure.

Cross section SEM images of the Kentucky #9 char particles are shown in Figure 1.20. Char bubble structure appears to be affected by the pressure. The char particles produced at lower pressure tend to have one or several large bubbles in the central area, with small bubble clusters appearing near the outer surface of the char particles (i.e., the char “skin”). For char particles produced at elevated pressures, bubbles are more evenly distributed throughout the particle interior, and the walls between pores are thinner than in the chars made at lower pressure. Similar phenomena can also be observed from Pitt #8 chars (see Figure 1.17). The observed phenomena can be explained using char structure evolution mechanism of Yu et al. (2002). The bubble structure of chars produced at lower pressure is in the later stage of structure evolution, and chars produced at higher pressure are in the early stage. The char structure evolution is restrained by elevated pressure. Considerable

amounts of volatiles are transported through bubble movement. Small bubbles are created during the initial stage of devolatilization, and then

Figure 1.19. SEM micrograph of char produced from pyrolysis of Ken #9 coal
(a) 1 atm, (b) 2.5 atm (c) 6 atm (d) 10 atm (e) 15 atm.

Figure 1.20. SEM micrograph of char cross section produced from pyrolysis of Ken #9 coal (a) 1 atm, (b) 2.5 atm (c) 6 atm (d) 10 atm (e) 15 atm.

these small bubbles merge together to form larger bubbles. The larger bubbles move to the particle exterior surface and finally burst open. At high pressure, transport of bubbles is more difficult, and a char with characteristics of the early stage of bubble evolution is produced. The char structure observed illustrates one possible reason for lower mass release at elevated pressure.

The effect of pressure on coal particle swelling ratio was discussed previously (Figure 1.14). Here the swelling ratios are interpreted using char morphology. Within the range of pressures tested in this study, the swelling ratios of all four coals studied increased with increasing pressure. The morphology of the Kentucky #9 char consistently illustrates the trend of increased swelling ratio with elevated pressure. At higher pressures, the char became more fluid because of the increased amount of metaplast. Bubbles were created and trapped within the particle by the increased resistance created by high pressure. These bubbles expanded and formed thinner inter-bubble walls, until a force balance was achieved with the reactor pressure exterior to the particle. At lower reactor pressures, bubbles merged or burst open because of a smaller mass transfer resistance compared to the high-pressure condition, thus forming thicker walls and blow holes on the particle exterior surface. Therefore, smaller swelling ratios were observed at the lower pressures, and even fragments in some particles were observed. This swelling effect is governed by many factors such as coal rank, heating rate, and pressure. These same types of effects were observed in the other bituminous coals studied in this experiment. In contrast, very few changes were observed in the morphology of Knife River lignite chars as a function of pressure, since lignites do not go through a softening regime.

1.4.7 Char Surface Area

The internal surface area of char is an important factor affecting the reactivity of char oxidation or gasification, but only a few studies have reported the effect of pressure on char surface area. Lee et al. (1992) found that chars generated at higher pressure have lower N_2 surface areas, and that CO_2 surface areas increase with pyrolysis time. Similar trends were also reported by Wall et al. (2002). In the contrast, Roberts et al. (2003)

found that both CO₂ and N₂ surface area increased with pressure during coal pyrolysis. CO₂ surface areas of chars were more sensitive to increases in pressure. In the current study, both CO₂ and N₂ surface areas of chars decreased with increasing pressure (see Figure 1.21). The CO₂ surface area was larger than the N₂ surface area at all pressures. CO₂ surface areas are usually representative of micropore surface, and N₂ surface areas are representative of meso and macropores. These trends mean that chars produced at high pressure have fewer micropores than low pressure chars. This trend is consistent with the SEM analysis, where high pressure chars exhibited more distinct bubbles than low pressure chars. This trend is consistent with the SEM analysis, where high pressure chars exhibited more distinct bubbles than low pressure char, and the texture of solid part of the char was denser and less porous.

Figure 1.21. Surface area of chars prepared at different pressures.

1.5 Chapter 1 Conclusions

Four coals with a broad rank distribution, including Kentucky #9, Illinois #6, Pitt #8, and Knife River Lignite, were pyrolyzed in an atmospheric flat-flame burner and a high-pressure flat-flame burner. Resulting chars were collected at pressures of 0.85, 2.5, 6, 10,

and 15 atm. The chars were analyzed to find the formation the effect of pressure on char properties.

The measured decreases in total volatiles yields with increasing pressure were predicted using the CPD model using only the elemental composition and ASTM volatiles yields of the parent coals as changeable input parameters that relate to coal chemical structure. The H/C and O/C ratios in the resulting chars initially increase with increasing pressure, but remain relatively constant at pressures from 6 to 15 atm. The H/C ratio in the char is thought to be affected by the decrease in tar yield at increased pressures, the change in the hydrogen content of the tar with pressure, and the increase in light gas yield as pressure increases. The change in residence time at different pressures in these experiments may also have played a role in the hydrogen release.

Swelling ratios of the lignite chars were less than 1.0, and only about 1.3-1.8 for the bituminous coals. All coal chars showed slight increases in swelling behavior as pressure increased. The swelling behavior observed for the Pitt #8 coal char at each pressure was lower than reported in high pressure drop tube experiments, supporting earlier work at atmospheric pressure showing that particle swelling decreases as heating rates approach 10^5 K/s. The morphology of chars produced at different pressures were analyzed using SEM. Chars formed at high pressure were in the early stage of foam structure evolution, while chars formed at low pressure were in later stages of foam evolution. The swelling ratio of chars increased with increasing pressure, and is attributed to bubble evolution.

Char surface areas using both CO_2 and N_2 as adsorption gases decreased with increasing pressure. The amount of micropores is less for chars produced at high pressure. These chars are more porous but have a denser framework.

CHAPTER 2 INTRINSIC REACTIVITY OF CHAR FORMED AT ELEVATED PRESSURE

2.1 Literature Review : Effect of Pressure on Resulting Char Reactivity

The pressure at which the parent coal is devolatilized also plays an important role in the reactivity of the resulting char. Sha et al. (1990) noted a significant decrease in the reactivity of the char as pressure was increased, postulating that reactivity was affected by changes in pore structure. Van Heek and Mühlen (1991) noted that the steam reactivity for chars is not affected by pressure if pyrolysis is performed under inert conditions. Under a hydrogen atmosphere, increased pressure resulted in a decrease in the steam reactivity of the resulting char. Cai et al. (1996) found combustion reactivities (calculated as the maximum rate observed during the conversion profile at 773 K) decreased during hydro-pyrolysis at pressures up to 40 atm and increased at pressures above 40 atm. The eventual increase in reactivity was reportedly the result of some char conversion by H₂ at the higher pressure, which exposed a fresh and enlarged carbon surface. Lee et al. (1992) investigated the structure and reactivity of Illinois No.6 coal char following pyrolysis at elevated pressure. They found that increasing the pressure slowed the rate of release of volatiles, increased the amount of char remaining after pyrolysis, and altered the composition of the volatile products. Their data also demonstrated how pressure hinders the development of the mesopore system that develops after the coal passes through the plastic phase of pyrolysis. The increased fluidity that resulted from higher-pressure pyrolysis led to enhanced ordering of carbon layers and the subsequent loss of gasification reactivity in the char residue.

Roberts et al. (2000) measured the apparent and intrinsic gasification rates of an Australian coal char collected from a pressurized drop tube furnace (PDTF) under various pressures. Char reactivity varied significantly with pressure, whereas the intrinsic rates, which were obtained by normalizing the apparent rate by internal surface area, were almost independent of pressure over a range of 1 to 15 atm. Comparisons of the initial apparent and intrinsic gasification rates of vitrinite- and inertinite-rich char samples from the same coal were given by Benfell et al. (2000). The inertinite-rich sample had a faster

apparent gasification rate than the vitrinite-rich sample when made at 5 atm, but a slower apparent gasification rate when made at 15 atm. However, it was shown that the intrinsic reaction rates of these char samples did not systematically show large variations with pressure or maceral concentrations in the parent coal. This suggests that the pressure significantly influences the physical structure of coal chars, as discussed above, but has little effect on the chemical structure of char, which largely determines the intrinsic char reactivity. Such a conclusion has significant implications for interpreting char reaction rates and mathematical modeling of char burnout.

In summary, chars produced at different pressures were reported to have different apparent reaction rates, but similar intrinsic rates. However, pressure may have a significant influence on char morphology. High pressure pyrolysis forms more porous char particles. The morphology contributes to the difference in apparent reactivity. Chemical structures of chars formed at different pressures seem similar, as long as the char preparation temperature is low. Further studies are needed to determine the effects of high pyrolysis temperatures (>1673 K) and high pyrolysis pressures on the properties of char.

2.2 Objective

The objective of this part of the project is to study the effects of pressure on the TGA (i.e., low temperature) oxidation rate of coal chars formed at high temperatures and high heating rates, typical of industrial pulverized coal combustion.

2.3 High Pressure Thermogravimetric Analyzer (HPTGA)

The Deutsche Montan Technologie (DMT) high pressure Thermogravimetric analyzer (HPTGA) (Figure 2.1) is an electrically-heated apparatus that allows the control of temperature, pressure, gas concentrations, and flow rates. A sample is placed in some type of basket that is suspended from a chain attached to the microbalance, and is lowered into the furnace. The weight of the sample is then measured and recorded

throughout the experiment by a computer. Time, temperature, and pressure are also recorded as a function of time. The temperature is monitored with thermocouples. Pressure is controlled by a PID controller, with an accuracy of $\pm 1\%$. The gas compositions and flow rates are controlled by mass flow controllers, with flow rates ranging from 0.1 to 10 L/min. The maximum reactor temperature is 1100°C. The maximum heating rate achievable in the reactor is 100°C/min. The entire vessel is rated at a maximum pressure of 100 bar. Some of the gases that have been used in the HPTGA include helium, nitrogen, oxygen, carbon dioxide, carbon monoxide, argon, hydrogen, and methane.

Figure 2.1. Schematic of the DMT high pressure Thermogravimetric Analyzer.

The HPTGA was characterized to ensure that the experiments were carried out under conditions such that the reaction rate was controlled only by chemical processes and was

not affected by mass or heat transfer effects. Temperature ranges, carrier gas, gas flow rates, and sample amount were chosen accordingly. Helium was chosen as the inert gas environment due to its high thermal conductivity and low density, which should minimize the thermal delay and buoyancy effects, and hence increase the accuracy of the data. A 4 mg sample size was used for all of the HPTGA tests and reported here.

2.4 Descriptions of HPTGA Tests

High-temperature, high-pressure pyrolysis experiments were conducted on three bituminous coal chars. Chars were collected at different pressures in the HPFFB. These chars were then oxidized using the same high-pressure Thermogravimetric Analyzer (HPTGA). Char intrinsic combustion reactivities were calculated based on mass vs. time data. This chapter will discuss the experiment procedure, the effect of pressure on resulting char reactivity, and reaction of mechanisms.

2.4.1 Char Preparation

Coal chars from Pitt #8, Ill #6, and Knife River Lignite were tested using the HPTGA. The properties of these coals were reported in the previous chapter. Chars were prepared using same procedure described in Chapter 1. All of the coals were pyrolyzed at 2.5, 6, 10, and 15 atm. Resulting chars were collected, and then stored in a refrigerator. Chars were dried at 110°C for 2 hours prior to each HPTGA test. The properties of these char were reported in the previous chapter.

2.4.2 HPTGA Test Procedure

TGA char oxidation experiments are usually conducted on small amounts of sample (~4 mg) in order to minimize bed effects. Careful characterization is needed to minimize the experimental error. The HPTGA used in this study was also used to conduct char combustion experiments at elevated pressure by Hecker et. al (2003). Based on their work, a certain experimental procedure was introduced to the current study to minimize the effect of buoyancy, flow rate, and gas composition, thus an intrinsic reactivity of char

oxidation which is free of mass transfer effects can be obtained. First of all, the total inert gas flow rate was set to 4 l/min. This flow rate was found to effectively minimize the effect of boundary diffusion, as well as conserve helium and facilitate pressure control in the reaction chamber. Second, helium was selected as the inert gas rather than nitrogen, because helium has significantly higher thermal conductivity than nitrogen. Third, samples less than about 4 mg were found to introduce weighing errors. Finally, gas compositions were carefully selected to avoid heating from char oxidation, and the reaction temperature was selected to be in the region of chemical reaction control.

Hecker et al. (2003) found that char intrinsic char oxidation rate, determined on a $(g_{\text{avail}}/(g_{\text{avail}})_s)$ basis, is independent of char burnout level, and that kinetic parameters are not affected by changes in total pressure. Char intrinsic char oxidation rate ($-r$), activation energy (E), and oxygen reaction order (n) were defined by an n -th order kinetic equation:

$$-r = Ae^{-\frac{E}{RT}} P_{O_2}^n \quad (2-1)$$

and found to be independent of the total pressure. It was been that the n th order kinetic model fits both atmospheric and elevated pressure char oxidation data very well, with $n = 0.7$ for both chars studied. The char studied by Hecker and coworkers were all formed at atmospheric pressure.

The results of Hecker et. al (2003) are consistent with some other studies (Suuberg et al., 1988). Since all the chars used in Hecker's experiments were produced at 1 atm, char intrinsic reactivity should have been essentially the same. However no experiments were performed to see if the char intrinsic reactivity changes if the chars were formed at different pressures. The experiments in the current study were performed precisely to study this effect. Table 2.1 shows the matrix of experiments performed in the HPTGA. For the three coals examined, chars were collected in the HPFFB at four total pressures (0.85, 6, 10, and 15 atm), and then tested at the same pressure in the TGA. Oxygen partial pressure and temperature were changed at each total pressure to find the char oxidation kinetic data. These conditions were carefully selected to minimize the effects of mass transfer and sample heating due to reaction.

Table 2.1 Matrix of Experiments in the HPTGA

	P _{Tot} = 1 atm	P _{Tot} = 6 atm	P _{Tot} = 10 atm	P _{Tot} = 15 atm
Pitt #8	✓	✓	✓	N/A
Ill #6	✓	✓	✓	✓
KNL	✓	✓	✓	N/A

2.4.3 Kinetic Analysis

Figure 2.2 shows a typical data set obtained from the HPTGA. The weight of the basket and sample is recorded continuously by the microbalance. These data were rescaled to the initial weight of sample (without the basket). The data were then fitted to an equation:

$$mass = A + Be^{\square C \square r} \quad (2.2)$$

The constants a, b, and c in equation 2.2 were obtained from a least squares analysis using Microsoft Excel. The oxidation rate of char was then calculated using:

$$\square r = \frac{1}{m_{avail}} \frac{dm_{avail}}{dt} \quad (2.3)$$

An example of the char oxidation rate is shown in Figure 2.3. The weight measurements in the HPTGA are not stable at the initial stages of experiment. The reactivity increases dramatically at burnout levels, as seen in Figure 2.3 for char burnout levels larger than 90%. This high reactivity is caused by using the available weight in the reactivity determination (Eq. 2.3).

Figure 2.2. Measured and fitted data set obtained from a HPTGA test.

Figure 2.3. Char oxidation reactivity as a function of burnout.

The reactivity can also be interpreted using following equation:

$$\bar{r} = \frac{dx_i}{dt} = \bar{r} \frac{1}{m_{initial}} \frac{dm_{avail}}{dt} \quad (2.4)$$

Figure 2.4 shows the same data processed using equation 2.4. The reactivity is not reasonable at the beginning of test because of instability of microbalance. The reactivity during the later stages of char burnout decreases to almost zero, which is caused by full consumption of the carbonaceous material. This data processing method can help to eliminate the problem of equation 2.3. However, in reality, the reactivity changes with burnout based on the remaining mass. Therefore, all HPTGA rate data were normalized by the instantaneous mass in this study (see Eq. 2.3).

Figure 2.4. Char oxidation reactivity as a function of burnout

There are wide variations in the methods used in the literature regarding how to interpret TGA data from char oxidation tests. Previous researchers have used average reactivity over a certain range of char burnout, maximum reactivity, initial char reactivity, or the reactivity at 20% burnout (Cai et al., 1996; Hecker et al., 2003; Roberts and Harris, 2000;

Roberts et al., 2003). Initial reactivities vary in an unpredictable manner due possibly to movement of the sample basket or slow degassing of a small amount of pyrolysis products. Therefore, in this study, reactivities are compared at TGA char burnouts between 20% and 60%. At the end of each TGA test, the sample was burned completely at higher temperatures and O_2 levels in order to determine the ash content for that sample. The sample and basket were then weighed on a separate, more accurate balance, to improve the accuracy of the reactivity data. Each TGA test was repeated three times. The average reactivity value and standard deviation value were computed from the repeat samples at intervals of 5% in the char burnout, and error bars were set at ± 2 standard deviations.

The activation energy and oxygen order of n-th order rate expressions of Pitt #8 coal and Ill #6 coals were also calculated. Activation energies were determined from standard Arrhenius plots ($\ln[\text{rate}]$ vs. $1/T$ at constant oxygen partial pressure). Oxygen reaction orders were determined from a power law model by determining slopes of $\ln[\text{rate}]$ vs. $\ln[P_{O_2}]$. The total pressure during these TGA tests was kept the same as the char formation pressure, so as to simulate a continuous combustion process. TGA conditions used here were temperatures ranging from 693 to 753 K and oxygen partial pressures ranging from 0.2 to 0.8 atm. The low temperatures ensure that intrinsic rates were measured. Resulting O_2 mole fractions were 20 to 50% for the 1 atm test, and lower than 13% for the 6, 10, and 15 atm tests. Low O_2 mole fractions are preferred to minimize the degree of char heating from the heat of the combustion.

2.5 Results and Discussion

2.5.1 Char Intrinsic Reactivity

The effect of pressure on the resulting char combustion reactivity is shown in Figure 2.5 for the Pitt #8 coal, Figure 2.6 for the Illinois #6 coal, and Figure 2.7 for Knife River lignite. Pitt # 8 chars were oxidized in the HPTGA at a partial pressure of O_2 of 0.32 atm and a temperature of 715 K. KNL char oxidation conditions were $P_{O_2} = 0.28$ atm and $T =$

615 K. The oxidation conditions of Ill #6 chars were $P_{O_2} = 0.4$ atm and $T = 693$ K. The temperatures and oxygen concentrations were low enough for each char to avoid mass transfer effects. All of the chars were oxidized at the same total pressure as their respective char preparation pressure (i.e., 2, 6, 10, and 15 atm). The different oxidation conditions for different coals were used to maintain a reasonable reaction time. For example, Knife River lignite is the lowest rank coal, so its reaction temperature and oxygen partial pressure were set lower than for the other coals.

Figure 2.5. Pitt #8 char oxidation reactivity as a function of burnout.

Figure 2.6. Ill #6 char oxidation reactivity as a function of burnout.

Figure 2.7. KNL char oxidation reactivity as a function of burnout.

As seen in Figure 2.5, each of Pitt #8 char reactivity curves is relatively constant for char burnouts from 30 to 60%. This region of constant char reactivity is consistent with results presented by Hecker et al. (2003), where chars produced at atmospheric pressure in a FFB were examined in a HPTGA.

Hecker's results also indicated no change in TGA O₂ reactivity for the same starting char as total pressure was increased. In contrast, Figure 2.5 shows that after 60% burnout, the 6 atm HPFFB char is observed to decrease in reactivity faster than the 1 atm FFB char. At this degree of char burnout, activated sites may have been mostly consumed and initial pore structure destroyed, causing char reactivity changes. The reactivity of the 10 atm Pitt #8 char is about 50% lower than the reactivities at the lower pressures. This decrease in reactivity with pressure differs from results reported previously in the literature (Roberts et al., 2003).

Figure 2.6 shows the char reactivity of Ill #6 char with burnout. In general, char produced from Ill #6 coal decreased in reactivity as the pressure during pyrolysis increased. This is consistent with the results from the Pitt #8 coal. The reactivity curve of

15 atm char became unstable above 50% char burnout, due to instability in the mass measurement. When the HPTGA was operated at high pressure, it usually took longer time for the microbalance to be stabilized after lowering the char sample basket into the furnace. As mentioned previously, the mass measured at the early stages of oxidation is not suitable for use in calculating the burnout rate. Therefore, the reported reactivities are theoretically from the early stages of burning, but actually are from partially reacted char samples.

Another interesting result from Figure 2.6, and from the 10 atm curve in Fig 2.5, is that char reactivity increases with increasing burnout rate. Since active sites were consumed when char oxidizes, the reactivity should decrease, especially at the late stage of burning. However the results obtained from these chars are apparently different. The effect of experimental uncertainty has been eliminated by repeating the tests at the same condition for different kinds of chars. One of the possible causes of this result may be the calculation of averaging, since the late burnout has larger error bars. Another way to comprehend this result is to remember that the reactivity is normalized by the current dry ash-free mass (see Eq. 2.3). When a small amount of sample was used in TGA test such as this study (3-5 mg), $m_{\text{available}}$ can be very small at the late stages of burnout, and approaches zero on an ash-free basis. This provides a high degree of uncertainty when the burnout rate is high. The value of dm/dt actually decreases at the late stages of burnout for all of conditions, but this decrease was counteracted by the change in m_{avail} . This effect can be controlled somewhat by increasing sample size, but then the extra combustion heat of combustion can simultaneously raise sample temperature.

Figure 2.7 shows that the lignite reactivities also decrease monotonically with increasing pressure. This is an interesting result, since the lignite char does not soften and resolidify during pyrolysis, and also since the effect of pressure on lignite pyrolysis yields are thought to be minimal. Explanations for this behavior are left for further studies.

The effect of pressure on resultant char reactivity has been studied under a variety of reaction conditions (Cai et al., 1996; Chitsora et al., 1987; Kajitani and Suzuki, 2003; Lee et al., 1992; Roberts et al., 2003; Sha et al., 1990; Van Heek and Muhlen, 1991).

Different pyrolysis atmospheres and temperature were used; char reactivities included oxidation rates as well as H_2O , and CO_2 gasification rates. Among them, three references (Chitsora et al., 1987; Kajitani and Suzuki, 2003; Sha et al., 1990) used high temperature (700-930°C) in their reactivity tests, and hence are not used for direct comparison since mass transfer may have affected their results. Roberts et al. (2003) pyrolyzed three Australian coals at 5, 10, and 15 atm. Char oxidation reactivities were measured at 10 or 15 atm at 723K in 50% O_2 . The initial reaction rate for one char increased with increasing pressure, while no clear trend with pressure was observed for two other chars. However, the reactivities after normalization by the char CO_2 surface areas were the same. Cai and coworkers (1996) examined chars formed during hydrolysis (i.e., pyrolysis in H_2) as a function of pressures. They found that Pitt #8 and Linby char combustion reactivities decreased with pressure at low to medium pressures (20-30 bar), then increased at increased pressures. Lee et al. (1992) found that Illinois char reactivity generally decreased with increasing char formation pressure, but that this decrease was not as significant for coal pyrolysis residence times longer than 1 s. Lee and coworkers found no correlation between the micropore surface area (CO_2) of chars and char oxidation reactivity.

Generally, at low to medium pressures (1-40 atm), most of these studies showed that char reactivity decreased as char formation pressure increased. One study found that char reactivity increased with increasing pressure. Increasing pressure is thought to decrease the tar yield, and hence increase the hydrogen content in the char. Increased hydrogen contents in char generally translate to higher reactivities. Increased hydrogen contents in the char at increasing pressure are generally observed. However, high-pressure also increases the fluidity of the char, making the char surface more ordered, which generally means lower reactivity. This resolidification process can also be affected by residence time, causing lower char reactivity (Lee et al., 1992). Char surface area may also contribute to reactivity change with pressure, and will be discussed later in this chapter.

2.5.2 Activation Energy and Oxygen Order in N-th Order Kinetic Rate Expression

A series of TGA experiments were performed to 1, 5, 10, and 15 atm Pitt #8 chars to determine reaction orders and activation energies, following the basic TGA test procedure of Hecker et al. (2003). Temperatures used in these TGA experiments ranged from 693 to 753 K, and oxygen partial pressures ranged from 0.2 to 0.8 atm. The low temperatures ensure that intrinsic rates were measured (i.e., negligible effects of heat and mass transfer). The reaction orders and activation energies were calculated based on the average reactivity from 20-60 % burnout. Resulting O₂ mole fractions were 20 to 50% for the 1 atm test, and lower than 13% for the 6, 10, and 15 atm tests. Low O₂ mole fractions are preferred to minimize char heatup from reaction. The reaction orders and activation energies determined from these experiments are shown in Table 6.2 Except for the data point at 6 atm, the activation energy stays roughly constant with total pressure, and the oxygen order stays relatively constant at 0.7, in agreement with Hecker's results (2003).

Table 2.2 Activation Energies and Oxygen Orders of Pitt #8 Coal Chars

Total Pressure (atm)	Activation Energy (kcal/mol)	Oxygen Order
1	29.15	0.78
6	18.90	0.64
10	37.76	0.74
15	30.86	0.73

Similar sets of TGA experiments were performed on the 1, and 6 atm Ill #6 chars to determine reaction orders and activation energies. TGA experiments were conducted at temperature ranging from 663-723.5 K and oxygen partial pressures ranging from 0.2-0.5 atm. The results show a large variation in order than for the Pitt #8 coal char.

Table 2.3 Activation Energies and Oxygen Orders of Ill #6 Coal Chars

Total Pressure (atm)	Activation Energy (kcal/mol)	Oxygen Order
1	29.85	0.67
6	23.26	0.84

2.5.3 The Relationship between Surface Area and Char Reactivity

The internal surface area of the char is an important factor affecting the reactivity of char oxidation or gasification. However, only a few studies have been reported that treat the effect of pressure on char internal surface area. Lee et al.(1992) found that chars generated at higher pressures have lower N₂ surface areas, and that chars exhibit larger CO₂ surface areas with increasing pyrolysis time. Similar trends are also reported by Wall et al.(2002) In contrast, Roberts et al. (2003) found that both CO₂ and N₂ surface area increased with increasing pressure during pyrolysis, and that CO₂ surface areas were more sensitive to the increases in pressure. In the current study, both CO₂ and N₂ surface areas of chars generally decreased with increasing pressure, as shown in Figure 1.21, with the exception of the Pittsburgh #8 data at 2.5 atm. Measured CO₂ surface areas were larger than the N₂ surface areas at all pressures. CO₂ surface areas usually correspond to micropore surface area (< 2 nm pore sizes), and N₂ surface areas correspond to meso and macro pores (2 to 50 nm pore diameters). The trends shown in Figure 1.21 and the SEM of chars shown in Figure 1.17 and 1.20 imply that chars produced at high pressure have fewer amounts of micropores than low pressure chars. Even though high pressure chars exhibit more distinct bubbles than low pressure chars in the SEM, the texture of the solid part of the high pressure char (i.e., the bubble wall) is denser and less porous.

Pressure effects on char reactivity can also be related to surface area, with either CO₂ or N₂ as the adsorption gas. The normalized reactivities are calculated using the following equation:

$$r_{\text{normalized}} = \frac{r_{\text{intrinsic}}}{A_{\text{CO}_2 \text{ or } \text{N}_2}} \quad (2.5)$$

where $A_{\text{CO}_2/\text{N}_2}$ is the CO_2 or N_2 surface area in m^2/g , respectively. The intrinsic reactivity $r_{\text{intrinsic}}$ is defined as:

$$r_{\text{intrinsic}} = \frac{1}{m_{\text{avail}}} \frac{dm_{\text{avail}}}{dt} \quad (2.6)$$

Intrinsic reactivity data obtained in a high pressure thermogravimetric analyzer (HP-TGA) for chars prepared in the HPFFB facility were reported on a dry, ash-free basis in a previous section. The intrinsic reactivity ($r_{\text{intrinsic}}$) can be viewed as an “overall” intrinsic reactivity, which includes contributions by both the char surface activity and the “available” reaction area. However, it is difficult to quantify these effects individually. By normalizing the reactivity by the char internal surface area, the effect of char surface property on reactivity can be determined. It was difficult to obtain the initial char reactivity at 0% char burnout because of instabilities at the beginning of each HPTGA experiment. The intrinsic reactivities of Pitt #8, Ill #6, and KRL coal char were therefore taken from the time at which 5% char burnout was achieved in the HPTGA. The surface areas used in the normalization were measured using the original char. These surface area values were assumed not to change after 5% char burnout at the low temperature conditions used in the HP-TGA experiments.

It is not clear in the literature which surface area measurement can be treated as the “available area” for char oxidation, even at the relatively low TGA reaction temperatures. Both N_2 and CO_2 surface areas were therefore used to reduce the data. The values obtained may not precisely reflect the true active surface area, but can provide a qualitative insight into the effect of char surface area on reactivity.

Figures 2.7-2.9 show HP-TGA reactivity data for the Ill #6, Pitt #8, and KRL coals, respectively. The intrinsic reactivity has units of $\text{g}/(\text{g}\cdot\text{sec})$ and was multiplied by 10^3 in this figure, while the normalized reactivity has units of $\text{g}/(\text{sec}\cdot\text{m}^2)$ and was multiplied by 10^5 in this figure for comparative purposes. For all coals, the reactivity normalized by CO_2 surface area was smaller than the rate normalized by N_2 , since the CO_2 surface area

is always larger than the N₂ surface area. The normalized reactivity remained relatively constant as a function of pressure for the Illinois #6 coal and the lignite for both the CO₂ and N₂ surface area; more pressure dependence was seen in the non-normalized intrinsic reactivity for these chars. The Pitt #8 char data at 2.5 atm showed one inconsistent data point for the reactivity normalized by the N₂ surface area, otherwise the normalized data showed a minimal change with pressure.

These results imply that the decrease in intrinsic char intrinsic reactivity is mainly due to changes in the internal surface area. Chars prepared at low pressure have larger internal surface areas available for low temperature oxidation. The temperatures used in the TGA experiments were low enough to minimize the effects of pore diffusion. Differences in char chemical structure, as indicated by the H/C and O/C ratios, can not explain the difference in reactivities observed at different pressures. This observation of the importance of internal surface area is somewhat consistent with the results of Roberts et al. (2003) However, in the current study, it is hard to distinguish the relative importance of CO₂ versus N₂ surface area, since almost the same trend was observed for

Figure 2.7. Ill #6 char reactivity and normalized reactivity.

Figure 2.8. Pitt #8 Char reactivity and normalized reactivity.

Figure 2.9. KNL char reactivity and normalized reactivity.

each surface area normalization. Further studies are still required to determine the correct available surface area that describes char oxidation as a function of pressure.

2.6 Chapter 2 Conclusions

A flat-flame burner was used in a high pressure laminar flow facility to conduct high temperature, high heating rate coal pyrolysis experiments. Particle heating rates were approximately 10^5 K/s, which is higher than in conventional drop tube experiments. Char samples from coals such as Pitt #8, Ill #6, Ken #9 coal, and lignite were collected at 1300°C at 2.5, 6, 10, and 15 atm.

TGA char oxidation reactivities were measured at the same total pressure as the char preparation pressure. The general trend was that the TGA reactivity on a gram per gram available basis decreased with increasing char formation pressure for both Pitt #8 and Knife River lignite coal chars. The Pitt #8 char intrinsic activation energy and oxygen reaction order remained relatively constant with increasing pressure.

The intrinsic char-O₂ reactivity was measured in a HP-TGA on a g/g_{avail}-s basis. The intrinsic reactivity at 5% char burnout was then normalized by either the N₂ or CO₂ internal surface area. The resulting normalized reactivity was found to be relatively constant with increasing pressure for both the N₂ and CO₂ normalizations. The reactivity that was normalized by the N₂ surface area was higher than that normalized by the CO₂ surface area, as expected. The fact that the normalized reactivity is constant with pressure strongly implies that the majority of the change in char reactivity with pressure can be attributed to changes in internal surface area.

CHAPTER 3 ELEVATED PRESSURE, HIGH TEMPERATURE COAL OXIDATION EXPERIMENTS AND MODELING

3.1 Literature Review

A review of published data from high pressure coal combustion and char oxidation experiments is listed in Table 3.1.

Table 3.1 Test Conditions for Various High Pressure Oxidation Rate Measurements

Investigator(s)	Fuel	diameter (μm)	T_p (K)	P_{total} (atm)	x_{O_2} (%)
Monson (1992)	chars	63-75	1300-2100	1-15	5~21
Mathias (1996)	Coals, chars	6, 9 mm	900-1300	0.86-5	6-18
Ranish and Walker (1993)	graphite	flakes	733-842	1-64	100
Banin et al. (1997)	chars	~6	1200-1800	8	0-100
Croiset et al. (1996)	chars	90-106	850-1200	2-10	1.5-10
Moors, J.H.J (1999)	char	<10	1300-3000	6-11	0-100
Roberts and Harris (2000)	chars	600-1000	723	15	50
Hecker et al. (2002)	chars	64-76	598-723	1-32	2.5-80

Monson (1992) investigated high-pressure and high-temperature char oxidation using a high-pressure controlled-temperature profile drop-tube reactor. The measurements were performed for Utah and Pittsburgh coals at reactor temperatures between 1000 and 1500 K and total pressures of 1, 5, 10 and 15 atm. At constant oxygen mole fractions (0.05, 0.10 and 0.21), increasing total pressure from 1 to 5 atm led to a slight increase in the reaction rate, with the rate decreasing with further increases in total pressure from 5 to 15 atm. Monson (1992) used a global n -th order char oxidation model to fit his data. The calculated apparent rate coefficients showed significant pressure dependence, since both the activation energy and frequency factor decreased with increasing pressure. Since these rate coefficients should not vary with pressure, this appears to show that the global n^{th} order approach is inadequate in modeling char oxidation rates when total pressure is varied.

Mathias (1996) performed oxidation experiments on char particles of mostly 8-mm diameter with a Cantilever Balance Attachment (CBA) in a drop tube reactor. The gas temperatures were 825, 1050, and 1200 K (measured by a type-S thermocouple 1.2 cm

above the particle). The gas velocities were 0.08, 0.32, and 1.28 m/s. The pressures tested were 0.86, 3.0, and 5.0 atm. Major findings included: 1) An increase in the partial pressure of oxygen resulted in a significant increase in the char oxidation rate on the runs performed at atmospheric pressure; 2) An increase in total pressure, while maintaining the same partial pressure of oxygen, drastically decreased the oxidation rate; 3) Increasing the total pressure from 0.86 and 5.0 atm while maintaining oxygen mole fraction at 21% produced a small increase in the oxidation rate; 4) Correlating the oxidation rate to the mole fraction of oxygen rather than to the partial pressure of oxygen better described the trends in the experimental data.

Ranish and Walker (1993) studied the oxidation rates of highly crystalline graphite flakes at oxygen pressures between 1-64 atm and temperatures ranging from 733-842 K. The global activation energy (defined as the slope of the log [reaction rate] vs. $1/T_p$ curve, the term “global” arising from the fact that the form of the reaction rate is unknown) for the reaction was found to be 204 ± 4 kJ/mole and was independent of carbon burnout. The intrinsic reaction order decreased from 0.83 to 0.69 as the reaction temperature increased from 733 to 813 K

Banin and Veefkind (1997) studied the combustion behavior of pulverized char in drop-tube experiments. The gas temperature was varied between 1200 and 1800 K and the gas pressure was about 8 atm. The oxygen partial pressure was varied between 0.3 and 8 atm. In all cases, 95% of the coal and char particles had diameters less than $6 \mu\text{m}$. The apparent reaction order at high oxygen pressure was observed to be as low as 0.3. This could not be explained as Zone I combustion since the char particles were observed to burn with shrinking diameters, and the particle temperatures (1480 ~ 2850 K) were beyond the temperature range where Zone I combustion typically occurs.

Croiset (1996) performed combustion experiments on Westerholt bituminous coal char in a fixed-bed reactor at 2, 6, and 10 atm and temperatures between 850 and 1200 K with particle diameters in the range of 90-106 μm . The reported reaction was first order in both Zone I and Zone II. The pre-exponential factor, A , decreased when the total

pressure increased from 2 to 6 atm. Above 6 atm, the effect of total pressure was very weak. High pressure also favored the combustion regime controlled by pore diffusion. Attempts were made to apply the Langmuir rate equation to these data. However, the mole fraction of oxygen was used instead of the oxygen concentration. The theoretical basis behind the use of between the mole fraction and concentration needs to be explored.

Moors (1998) investigated combustion of Göttelborn char in a high temperature and high pressure shock tube. The particle temperature varied between 1300-3000 K. The total gas pressure varied between 0.6-1.1 MPa. He concluded that the combustion of Göttelborn char particles occurs in the rough-sphere regime (defined by Moors as regime in which the external surface area of the particle is much larger than the internal surface area involved in the combustion process). The penetration of oxygen into the pores was small. Internal transport of reactant had no influence on the apparent kinetics. Based on an energy balance, a mass balance and a carbon dioxide production calculation, the kinetics were found to be of a Langmuir type. Adsorption of oxygen at active sites determines the overall reaction rate at partial pressures higher than about 0.4 MPa. The reaction order decreased from unity to zero when the oxygen partial pressure increased. When internal transport influenced the apparent combustion kinetics, the reaction order decreased to one half as the pressure increased. Moors also found that the particle size distribution and the temperature history of the particles influenced the kinetic reaction rates obtained. The shock tube gave smaller activation energies than other reactors. This difference was due to a difference in burnout time and a more pronounced influence of thermal annealing for the reactors with a longer burnout time.

Roberts (2000) measured the intrinsic reactivities of two Australian coal chars (produced at 1100°C nitrogen for 3hr) to O₂, CO₂, and H₂O at pressures up to 30 atm. Measured reaction orders in CO₂ and H₂O were not constant over the pressure range investigated, whereas reaction order in O₂ was unchanged. The differences in reaction order transition appeared to be related to the rate of the reaction. Activation energies of all three reactions were not found to vary as the pressure was increased. These results demonstrated that a physical rather than a chemical change is the reason for the observed variations in the

apparent reaction order. However, the authors pointed out a need for high-temperature high-pressure measurements of reactivities in order to validate their conclusion.

Hecker et al. (2003) examined the intrinsic oxidation of two coal chars prepared at high temperature and high heating rate at atmospheric pressure. High pressure TGA experiments were conducted over a pressure range of 1 to 32 atm, a temperature range of 598 to 823 K, a range of oxygen partial pressures from 0.03 to 12.8 atm, and a burnout range of 20 to 60%. Under these conditions, it was found that intrinsic char oxidation rate, determined on a g/g_{actual} -s basis, was independent of char burnout level, and that kinetic parameters were not affected by changes in total pressure. More specifically, under the conditions of this study, intrinsic char oxidation rate, activation energy, and oxygen reaction order were found to be independent of total pressure. It was also reported that the n th order kinetic model fits both atmospheric and elevated pressure char oxidation data very well, with $n = 0.7$ for both chars studied.

In summary, elevating reaction pressure increases char oxidation reactivity. The reaction rate may be almost independent of total pressure at total high pressure. Char oxidation rates at elevated pressure may increase with an increase in total pressure from atmospheric pressure to almost 10 atm, and then reduce at even higher pressure.

More work should be performed in order to firmly establish the kinetics of high pressure char oxidation. One particular area that should be studied is the intrinsic kinetics of chars produced at elevated pressure. Chars produced at elevated pressures may exhibit different behavior compared to chars produced at atmosphere pressure. In addition, it is possible that the internal surface area of the char changes significantly as experimental conditions vary. Many mechanistic models of intrinsic reactivity normalize the reactivity by the internal surface area. Changes in the internal surface area may account for the changes in reactivity with total pressure or burnout predicted by some of these models. Finally, high temperature, high pressure char reactivity data are needed.

3.2 Objectives

The objectives of this chapter are: (1) obtaining the char high temperature, high pressure reactivity data, (2) modeling of char combustion process using char burnout kinetic model (CBK).

3.3 Conditions of Combustion Tests

3.3.1 Coal Selection

Coal oxidation experiments were performed with three fuels: two size fractions of Pittsburgh #8 (63-76 μm , 90-125 μm) and one size fraction of Illinois #6 (74-90 μm). These are common U.S. coals that have been widely studied in char oxidation experiments. Samples of the coals were ground, dried and stored in refrigerator before experiments.

3.3.2 Experimental Conditions

All of elevated pressure coal combustion experiments were conducted using the methane-air high-pressure flat flame burner (HPFFB) that is described in Chapter 1. Three kinds of Coal were injected into the HPFFB, varying O_2 concentration, residence time, and total pressure.

The previous high-pressure char combustion experiments (Banin and Veefkind, 1997; Croiset et al., 1996; Mathias, 1996; Monson, 1992; Monson et al., 1995; Moors, 1998; Ranish and Walker, 1993) were usually conducted using char formed at atmosphere pressure. The use of the same starting char was convenient for char kinetic analysis. Unfortunately, this approach neglected changes in the characteristics of the chars due to pressure. Several char oxidation kinetic models have been developed and applied to explain several sets of high-pressure char oxidation data (Hong et al., 2000; Niksa et al., 2003). This study will only compare previously-developed models to the char oxidation data obtained in this project.

In this study, parameters such as coal type, coal size, total pressure, bulk oxygen composition, and reaction distance were varied during the experiments. Two sizes of Pitt #8 coal were tested. Samples of Ill #6 coal char were collected at two reaction distances to test residence time effects. The test matrix for all of the coal oxidation experiments conducted is shown in Table 3.2.

Table 3.2 Matrix of Coal Oxidation Experiments^a

	P _{Tot} = 1 atm	P _{Tot} = 6 atm	P _{Tot} = 10 atm
Pitt #8 (63-76 m)	0-19.24 % O ₂	0-9.76 % O ₂	N/A
Pitt #8 (90-125 m)	0-19.24 % O ₂	0-9.76 % O ₂	0-11.97 % O ₂
Ill #6 (74-90 m) (ST*)	0-15.13 % O ₂	0-9.76 % O ₂	0-8.69 % O ₂
Ill #6 (74-90 m) (LT**)	0-15 % O ₂	0-12.4 % O ₂	N/A

* Short reaction distance

** Long reaction distance

^aall concentration are given in mol%

The post-flame O₂ concentration was adjusted by changing the CH₄/air ratio. The desired flow rates of each gas were first calculated using an equilibrium code such as NASA-Lewis code, and were controlled by adjusting the mass flow controllers. The oxygen concentration for each condition was examined using an O₂ monitor.

3.3.3 Gas Temperature Profile

The particle residence time is an important factor affecting the char burning rate. The reaction length was determined by measuring the distance from the burner to the collection probe.

Gas temperature profiles were measured for each reaction condition before char collection experiments were conducted. At each pressure, the flow rates of CH₄ and air were held constant, and the O₂ flow rate was adjusted to control the post-flame O₂

concentration. The flow rates of CH₄, air, and O₂ used in different experiments are shown in Table 3.3. Thermocouple measurements of gas temperature were adjusted for the effects of radiation, and are shown in Fig 3.1. These temperature profiles show two characteristics: (1) the dramatic decrease of temperature versus distance from about 1700 K to 1000 K at 2.5 atm, or to 700 K at 10 atm; and (2) the fact that gas temperature remained relatively constant at a given pressure when the O₂ concentration was changed from 0-15 mol%.

Table 3.3 Gas Flow Rates Used in the HPFFB

	Post flame O ₂ concentratio	CH4 (l/min)	Air (l/min)	O2 (l/min)
1 atm	5.75%	1.74	16.55	1
	9.76%	1.74	16.55	2
	15.13	1.74	16.55	3.3
6 atm	2.98%	2.16	20.5	0.7
	4.97%	2.16	20.5	1.25
	9.76%	2.16	20.5	2.5
	12.44%	2.16	20.5	3.3
10atm	4.97%	2.49	23.5	1.25
	5.67%	2.49	23.5	1.6
	9.76%	2.49	23.5	2.5
	9.86%	2.49	23.5	2.9

* All concentrations are given in mole percent.

Figure 3.1. Measured gas temperature profiles in the HPFFB at different pressures and oxygen concentrations.

3.4 Results and Discussion

3.4.1 Variations in Char Properties during Combustion

Figures 3.2-3.5 show the mass release for four sets of coal combustion experiments vs. O₂ molar fractions at different pressures. Mass release is reported here based on (a) the parent daf coal (solid lines), and (b) the initial char collected at 0.5% O₂ (dashed lines). The change in char properties vs. post-flame O₂ concentration for a given is thought to be small.

Figure 3.2. Measured mass release of Pitt #8 coal (90-125μm) during combustion experiments at different pressures and O₂ concentrations. Open symbols represent the data on a %char burnout basis, whereas closed symbols are normalized to the initial amount of dry ash-free coal.

Figure 3.3. Measured mass release of Pitt #8 coal (63-76μm) during combustion experiments at different pressures and O₂ concentrations. Open symbols represent the data on a %char burnout basis, whereas closed symbols are normalized to the initial amount of dry ash-free coal.

Figure 3.4. Measured mass release of Ill #6 coal (short reaction distance) during combustion experiments at different pressures and O_2 concentrations. Open symbols represent the data on a %char burnout basis, whereas closed symbols are normalized to the initial amount of dry ash-free coal.

Figure 3.5. Measured mass release of Ill #6 coal (long reaction distance) during combustion experiments at different pressures and O_2 concentrations. Open symbols represent the data on a %char burnout basis, whereas closed symbols are normalized to the initial amount of dry ash-free coal.

Unfortunately, due to the constraint of achieving similar temperature profile, the residence times varied for each pressure conditions. This also changes the particle

temperature profile. All of these factors made it difficult to interpret the mass release data directly, and hence the mass release data were modeled using the CBK model.

Figure 3.6 shows of N_2 BET surface areas of chars collected at different post-flame O_2 conditions and pressures. In this study, higher O_2 concentrations corresponded to higher extent of burnout (Figures 3.2-3.5) and lower N_2 surface areas. As shown for the Pitt #8 chars, the N_2 surface areas initially increase vs. O_2 concentration for some pressure conditions and then decrease at elevated pressures.

Figure 3.6. Nitrogen surface areas of char particles during combustion experiments at different pressures and O_2 concentrations.

No such initial increase in N_2 surface area was observed for the Ill #6 coal chars, or for some of the pressures for the Pitt #8 coal chars. For Ill #6 coal at both long and short residence time experiments, N_2 surface areas decrease with the increase of burnout. The change of char surface area with burnout is related to the evolution of pore structure. For the Pitt #8 coal chars, the opening of closed-off pores contributes to the initial increase of

surface area, followed by decreases in surface area due to the merging and coalescing of pores (Mitchell, 2003). The evolution of pore structure with burnout of Ill #6 coal did not display the initial increase, possibly caused by the different character of pore structure. Values of d/d_0 for the char samples, determined based on the initial coal diameter, are plotted versus the O_2 concentrations in Figure 3.7. The values of d/d_0 are calculated using the same method described in Chapter 2, which assumes a constant packing ratio. Values of d/d_0 , calculated based on the char produced at 0.5 mol% O_2 , are plotted against char burnout in Figure 3.8. The particle diameter ratio swelling ratio based on coal decreased with increasing O_2 concentration for all four conditions. For the Pitt #8 coal, the larger size coal reached a larger diameter ratio than the smaller size coal. The swelling ratio based on the char generally decreased with increasing char burnout. However, values of

Figure 3.7 Diameter ratios of char particles during combustion experiments at different pressures and O_2 concentrations. The initial coal diameters were taken from measurements of unreacted coal.

Figure 3.8 Diameter ratios of char particles during combustion experiments at different pressures and O_2 concentrations. Initial char diameters for normalization are taken from char formed at 0.4 mol% O_2 concentration.

d/d_{char} greater than one were obtained, such as for the Pitt #8 90-125 μ m char. This is possibly caused by the uncertainty of experiment condition, or the effect of varying O_2 content. In contrast, the diameter ratio (based on coal) of Ill #6 char in Figure 3.7 decreased quickly with increased O_2 concentration, and the diameter ratio based on char decreased to 0.5 at about 85% burnout, regardless of the experimental condition or the O_2 concentration.

3.4.2 Modeling of Gas and Particle Temperature Profiles

The gas and particle temperature profiles are critical in order to precisely model the char oxidation process. Gas temperature and particle velocity profiles for each condition were modeled using FLUENT. The centerline gas temperature profile for each condition was measured and used to validate the reliability of modeling results. The model assumed that

the inlet natural gas is reacted instantaneously to equilibrium. The composition of post-flame products was modeled using an equilibrium code, and was then used as input parameters in the FLUENT calculation. The geometry of the FLUENT modeling is shown in Figure 3.9. The reaction tube length is 321 mm, and the radius is 25 mm. The radius of the feeding tube is 2.38 mm.

Figure 3.9. Geometry and particle trajectory used in the FLUENT calculations.

Coal particles entrained by N_2 entered the reaction zone through a centerline feed tube. The average inlet radial entrance location of particles is assumed to be the area-averaged radius of the feeding tube, which is 1.68 mm from the centerline. Since the particle temperature is affected by the injection position, the area-averaged is reasonable based on the assumption that the particle is evenly distributed in the entraining N_2 flow. The primary gas velocity was set close to the secondary velocity in these experiments to minimize the radial dispersion of the particle. Observations of the particle trajectory at the outlet of the reaction tube indicated that particles flowed along the centerline. In this study, several coal particle size ranges were used, which includes 63-76 μm , 90-125 μm , and 74-90 μm . Average particle sizes of 69.5 μm , 107.5 μm , and 82 μm were used in the modeling. Since coal (not char) was used in combustion experiments, it is important to model both the pyrolysis and combustion reactions. In this study, the CPD model was used to calculate the time needed for coal pyrolysis. The combustion process was

assumed to begin after the end of pyrolysis. The particle velocity profile was partitioned accordingly.

Figure 3.10 compares the modeled gas centerline temperature profile with the measured temperature profile at 6 atm. To simulate the dramatic heat loss occurred at elevated pressure, wall temperature was decreased with increasing reaction length. By adjusting the wall temperature profile, good agreement was achieved between the modeled and measured gas centerline temperature profile. Once the gas temperature was modeled correctly, the velocity profile from the model was used. The modeled gas temperature profile is comparable with measured temperature profile, except for the temperature point closest to the burner. This is possibly caused by a departure of the thermocouple bead from the centerline.

Figure 3.10. Measured and predicted centerline gas temperature profiles for Pitt #8 coal at 6 atm.

Figure 3.11 shows the calculated particle velocity profiles of Pitt #8 (90-125 μ m) at pressures of 2.5, 6, and 10 atm. The velocity decreased dramatically with increased pressure because the gas has a higher density at elevated pressure. In the experiment, the flow rate of inlet gas was increased somewhat to compensate for the decrease in gas velocity. However the compensation was limited because of the necessity (a) to maintain the laminar flow pattern of the reaction gas flow, (b) to stabilize the flat flame, and (c) to

achieve a similar gas temperature profiles. These limitations made it impossible to perform experiments at isothermal conditions and similar residence times. The calculated temperature and velocity profiles were therefore used in char combustion modeling, and transient calculations were performed.

Figure 3.11. Predicted centerline particle velocity profiles for Pitt #8 coal.

3.4.3 High Temperature Char Combustion Modeling

3.4.3.1 Modeling of char combustion process using n-th order kinetic

The n^{th} order kinetic expression, also known as the power-law kinetic expression, usually has a form:

$$r_{gas} = kP_{O_2}^n = A \exp(-E / RT) P_{O_2}^n \quad (3.1)$$

This is the most widely used kinetic form in engineering calculations to account for the oxidation of carbon:

This simple reaction actually exhibits complex kinetic behavior. Among the many kinetic forms published, the n-th order kinetic expression is the simplest form. This form has often been criticized due to its lack of theoretical foundation. Consistent power law behavior was observed in several TGA studies (Hecker et al., 2003; Suuberg et al., 1988), but power law behavior failed to predict the char combustion behavior at high

temperature and high pressure (Monson et al., 1995). Recently, Hurt and Haynes (2004) postulated that surface chemical heterogeneity may result in n-th order kinetic behavior.

In this section, n-th order kinetics were used to model the high-temperature, high-pressure coal combustion kinetic data obtained in this project. Char Burnout Kinetics model 8 (CBK8) was used to model the char combustion process. CBK8 is a kinetics package that describes char oxidations relevant to pulverized fuel combustion processes (Hurt et al., 1998) that uses n-th order intrinsic kinetics. In addition, a separate version of Hurt's model that includes a e-step surface mechanism (CBK/E) was also used (Niksa et al., 2003).

Both CBK8 and CBK/E incorporate a new correlation for the coal swelling ratio (Benfell, 2001):

$$Sw_1 = \begin{cases} 8.67 - 0.0833C_{daf}, & 89 \leq C_{daf} \leq 92 \\ 0.0458 + 0.01459C_{daf}, & 72 \leq C_{daf} < 89 \\ 1.0, & C_{daf} < 72 \end{cases} \quad (3.3)$$

Where C_{daf} denotes the daf carbon content of parent coal, and Sw_1 represents the swelling ratio at atmospheric pressure. A correlation which involves the effect of operating pressure is:

$$Sw = \begin{cases} Sw_1^{0.7143+2.857P_T}, & 0.1 \leq P_T \leq 0.8 \\ Sw_1^{3.5[0.625P_T]}, & 0.8 \leq P_T \leq 4.0 \end{cases} \quad (3.4)$$

where P_T is the total pressure in MPa.

Figure 3.12 shows the comparison of the swelling ratios during devolatilization for Pitt #8 and Ill #6 coals that were measured vs. the values calculated using Benfell's correlation. The results from Benfell's model overestimate the swelling ratios of Pitt #8 and underestimate the swelling ratios of Ill #6. This discrepancy is possibly caused by the fact that this correlation does not account for heating rate. Due to the lack of agreement, the measured swelling ratios were used in the char combustion modeling, instead of using the correlation of Benfell.

In the CBK8 model, the initial starting char mass subsequent to pyrolysis is input via a variable named “high-temperature volatile yield (HTVL)”. However, starting char mass changes with pressure. The most rigorous modeling effort is to integrate a complex coal devolatilization model. In this study, coal particle temperature and velocity profiles obtained from FLUENT calculations were used as input for the CPD model. The coal pyrolysis time and volatile yield were calculated from the CPD model calculation and used as input parameters in the char combustion modeling.

Figure 3.12. Comparison of swelling ratios of Benfell's model and measured swelling ratios during devolatilization.

CBK8 uses an n-th order relation to calculate the CO/CO₂ ratio, and this relation was used here. The distributed activation energy model of thermal annealing and the ash inhibition model in the CBK models were also used. The CBK models were developed from coals similar to those used in this study and are therefore thought to be applicable.

The n-th order combustion model of char has three parameters: (1) the pre-exponential factor A, (2) the activation energy E, and (3) the Oxygen order n. The Oxygen order n

was assumed to be 0.5 based on Hurt's recommendation (1998). The pre-exponential factor A was correlated with coal carbon mass fraction, and was calculated as follows:

$$A = 10^{14.969 - 0.746 C_{daf}} \quad (3.5)$$

The values of the pre-exponential factor (A) were calculated for the two coals used in this study, are shown in the Table 3.4:

Table 3.4 Pre-exponential Factor (A) Used in CBK8

Coal	A (g/(g*sec*(mol/m ³) ^{0.5}))
Pitt # 8	3.214×10^8
Ill # 6	1.019×10^9

Using a single pre-exponential factor for each coal provides a basis for comparing char reactivity, which is reflected by the activation energy only. The activation energy E was optimized to find the best fit to the measured burnout data. Figure 3.13 shows a parity plot of the predicted vs. measured burnouts using CBK8. Figure 3.14 is the activation energies (E) used to obtain the best fit of the experimental measurements.

Figure 3.13. Predicted burnouts using of CBK8 versus measured burnouts for the four combustion conditions.

The resulting error between the modeling results of CBK 8 and the measured values of mass release or each coal char are listed in Table 3.5. The relative error is calculated using following equation:

$$\text{Relative error} = \sqrt{\frac{\sum_{i=1}^n (p_i^p - p_i^0)^2}{n}} \quad (3.6)$$

where n is the number of the records modeled; p_i^p is the prediction for the i^{th} record; p_i^0 is the measured value.

Figure 3.14. Modeled Activation Energy (E) of the best fit for the different pressures.

Table 3.5 Error between Calculations and Measured Values of Mass Release

Coal chars	Error (%)
Pitt #8 large	7.98
Pitt #8 small	8.08
Ill #6 long reaction distance	7.09
Ill #6 short reaction distance	18.20

3.4.3.2 Modeling of Char Combustion Process using 3-Step Kinetics

The Char Burnout Kinetics Extension model (CBK/E) was developed by Hurt et al. (1998), and then was later modified to include a three-step kinetic (Hurt and Calo, 2001):

This model was recently evaluated by comparison with several sets of high-pressure char combustion data (Niksa et al., 2003). Using one adjustable kinetic parameter A_{30} (pre-exponential factor of reaction 3.9) and default values for all other parameters, the model was shown to agree with the reported combustion behavior in many experiments. However, for low-rank coals, the values of A_{30} at high pressure are lower by just over half an order-of-magnitude than those at atmospheric pressure.

In the evaluation of CBK/E (Niksa et al., 2003), all of the data were obtained from combustion experiments on chars produced at atmospheric pressure. In contrast, the major objective of this study is to perform experiments on chars at the same pressure at which they were formed. The char burnout data (Figures 3.2-3.5) are modeled in this section using the CBK/E model.

In the CBK/E model, the char oxidation mechanism includes three reactions Eq. 3.7-3.9. Each reaction is a quasi-global reaction and has a pre-exponential factor A and an activation energy E . The overall rate and CO/CO_2 ratio are controlled by these parameters as follows (Hurt and Calo, 2001):

$$r = \frac{k_1 k_2 P_{O_2}^2 + k_1 k_3 P_{O_2}}{k_1 P_{O_2} + k_3 / 2} \quad (3.10)$$

$$CO / CO_2 = \frac{k_3}{k_2 P_{O_2}} \quad (3.11)$$

Among the six parameters A_1 , A_2 , A_3 , E_1 , E_2 , and E_3 , all activation energies were assigned based on the published char kinetic data (Niksa et al., 2003). The initial pre-exponential factor for k_3 (Step 3) is used to normalize the pre-exponential factors k_1 and k_2 . Thus the controlling parameter for three-step mechanism is the value of pre-exponential factor of reaction 3.9 (A_{30}). The values of E_1 , E_2 , E_3 , and A_{20}/A_{30} , A_{30}/A_{10} are listed in the Table 3.6.

Table 3.6 Kinetic Parameters Used in CBK/E

E_1 (kJ/mol)	25
E_2 (kJ/mol)	117
E_3 (kJ/mol)	133.8
A_1/A_{30}	1.0×10^6
A_2/A_{30}	5.0×10^4

The CBK/E model also uses a generalized internal effectiveness factor and a power-law exponent that relates density changes to the extent of burnout. Proper values were assigned to the kinetic and other submodels. The CBK/E model was included as a subroutine in an optimization software package OptdesX (Parkinson et al., 1992) in order to adjust the kinetic parameters (A_{30}) within pre-set values between 1.0×10^7 and 1.0×10^9 (Niksa et al., 2003) to best fit the experimental data.

Figure 3.15 shows the resulting comparisons of calculated and measured burnouts for the four conditions: Pitt #8 large particle size; Pitt #8 small particle size; Ill #6 short reaction distance; and Ill #6 long reaction distance. Because A_{30} is coal rank dependent and is also affected by the char formation pressure, a unique A_{30} was calculated for different pressures at each condition by minimizing the square error between model predictions and the data.

Effectively, A_{30} represents the “reactivity” of the char, and CBK/E does not have a mechanism to deal with the effect of pressure on char characteristics. Therefore, the variation of A_{30} is a measure of the effect of formation pressure on char reactivity.

The resulting errors associated with the best fit coal burnout results from CBK/E at different conditions, as shown in Figure 3.15, are listed in Table 3.7. The optimal values of A_{30} with pressure are shown in Figure 3.16.

Table 3.7 Error of the CBK/E model results

Coal chars	Error (wt%)
Pitt #8 large	10.44
Pitt #8 small	8.99
Ill #6 long reaction distance	7.88
Ill #6 short reaction distance	20.23

Figure 3.15. Predicted burnouts using CBK/E versus measured burnouts for the four combustion conditions.

Figure 3.16. Best-fit values of A_{30} for the four combustion conditions.

3.4.3.3 Discussion

Both an n^{th} -order (CBK8) and a 3-step surface mechanism (CBK/E) were used to model char combustion for two coals as a function of pressure. The n^{th} -order modeling results indicated that activation energies decreased by about 20% as pressure increased from 20 to 10 atm. The values of E calculated were within the range of 100 to 180 kJ/mol (24~43 kcal/mol), which is the range of reported activation energy in the most char oxidation experiments. The decreased activation energy with elevated pressure represents the increasing reactivity with increasing pressure.

Drastic changes in activation energy with pressure were reported by Monson et al. (1995), although their results were influenced by using chars formed only at atmospheric pressure and by the limitations of their 2-color pyrometer. It is not clear that the n^{th} -order kinetic model is correct, and hence a more mechanistic model was also used.

The CBK/E model was compared with the high pressure char oxidation data obtained in this project. Only one adjustable parameter (A_{30}) was used in the CBK/E calculations, with reasonable results. However, a different value of A_{30} was needed for each experimental condition for each coal, indicating that the effect of pressure on char properties affected reactivity as well.

The effect of the total pressure on char oxidation kinetics has been studied for decades, and the reported results do not seem consistent. Several reviews (Hong, 1999; Niksa et al., 2003; Wall et al., 2002) and the literature review of this chapter summarize the previous elevated pressures char oxidation studies. The char oxidation data available for comparison to this study have to meet the requirements such as high-temperature (Zone II temperature), pulverized coal size ($<100 \mu\text{m}$), and single particle behavior. Among the data that meet these criteria are:

1. Monson (1992), who reported that char oxidation rate increased with increasing pressure from 1-5 atm, then decreased at pressure from 5-15 atm;
2. Joutsenoja et al. (1999) and Saastamoinen et al. (1996), who reported that char burnout rate decreased at elevated total pressure
3. Cope et al. (1989) and Wall et al. (1999), who found that increasing total pressure increased the char oxidation rate.

Though it is not the mission of this study to analyze these data, comprehensive analysis can be found in three reviews (Hong, 1999; Niksa et al., 2003; Wall et al., 2002). The diversity of different results may be caused by the experimental technique and/or the respective data analysis.

It is well-known that char burnout is a function of char properties (e.g., ρ , pore structure and evolution, internal surface area, and elemental composition), reaction kinetics, and reaction conditions (e.g., P_{O_2} , T_p , and P_{tot}).

Several theoretical factors play roles in the change of char reaction rate with increasing pressure:

1. Bituminous coal chars undergo a plasticity stage during pyrolysis, thus char

formed at high pressure has a more oriented surface (Niksa et al., 2003) and lower surface area, which is associated with lower reactivity.

2. Char formed at high pressure has higher hydrogen content, which may be related to more reactive char.
3. Elevated total pressure can restrain the gas diffusion coefficient, thus decreasing the reactivity at high temperature (Zone II or Zone III combustion).
4. At constant total pressure, increased oxygen partial pressure (P_{O_2}) can increase the char oxidation reactivity until the char surface is saturated. At high temperature, a higher P_{O_2} is needed to achieve surface saturation because of the increased reaction rate (or faster desorption of surface complexes) (Roberts and Harris, 2000).
5. The effect of mineral matter is primarily responsible for the high-reactivity of low-rank coal, especially at low temperatures, although this effect becomes less important at high temperatures. The role of catalytic mineral matter at high pressure is still unclear (Niksa et al., 2003).

The complexity of char combustion reactions makes it difficult to develop a comprehensive model to including all mechanisms. The CBK/E model was a good attempt at using a surface mechanism, but still required one adjustable parameter A_{30} that was a function of pressure. Hurt developed correlations for A_{30} based on pressure and coal type, but notes that a complete mechanistic description is still unavailable (Niksa et al., 2003). However, this mechanism (in CBK/E) may be useful for engineering calculations.

3.5 Chapter 3 Conclusions

High-pressure, high-temperature char combustion experiments were performed in a HPFFB for two coals: Pitt #8 and Ill #6. Char samples were collected and analyzed. The following phenomena were observed:

- (1) Within the total pressure range from 2.5 to 10 atm, char burnout increased with increasing O_2 concentration at constant total pressure.
- (2) N_2 surface areas for Pitt #8 chars increased at early stages of burnout and then decreased with increasing burnout. N_2 surface areas for Ill #6 chars always decreased with increasing burnout. The evolution of pore structure with burnout contributed to the change of N_2 surface area. The difference in the surface area behavior between the two coals may be caused by the different character of pore structure.
- (3) The particle diameter ratio based on coal ($d/d_{coal,0}$) decreased with increasing O_2 concentration for all four conditions. For the Pitt #8 coal, the larger size coal achieved a larger swelling ratio than the smaller size coal. The diameter ratio based on the char ($d/d_{char,0}$) generally decreased with increasing char burnout. The diameter ratio (based on coal) of Ill #6 char decreases quickly with increased O_2 concentration, and the diameter ratio based on char decreased to 0.5 at about 85% burnout rate, regardless of the experimental condition or the O_2 concentration.

The gas temperature and velocity profiles were modeled using Fluent. The coal pyrolysis process was modeled using the CPD model. The results from these two models were used as input parameters for the char burnout model. Both n^{th} -order kinetics and 3-step surface kinetics were used to model the experimental results. Only one kinetic parameter was used to fit the experimental char burnout data:

1. Activation energy (E) was used as a fitting parameter for the n^{th} -order kinetic model (CBK8), and

2. A_{30} was used as a fitting parameter for the 3-step model (CBK/E).

Both CBK8 and CBK/E achieved reasonable agreement with the char combustion data. The modeling results showed that the char oxidation rate increased with increasing total pressure. A different value of E or A_{30} was necessary for each pressure condition for each coal. This means that a one-point calibration is necessary for every condition before CBK/E or CBK8 is capable of predicting char burnout.

The result obtained here that char reactivity increases with increasing total pressure is different than reported by some investigators. Some of that difference may be due to the fact that many previous investigators produced their starting char at atmospheric pressure only, rather than at the pressure where reactivity was measured (as was done in this study).

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CHAPTER 4

DEVELOPMENT OF A NEW SEMI-GLOBAL RATE EXPRESSION FOR CHAR COMBUSTION MODELING

Introduction

Advanced energy systems will operate over a wider range of temperature, pressure, and oxygen concentration than existing pc-technology. For this reason a more robust and widely applicable rate expression may be required for char combustion modelling in these systems. In this chapter we describe work done on this project targeted at the development and testing of such a new rate expression.

Background

The carbon-oxygen reaction has been described as "arguably the most important reaction known" [1], and indeed it plays an important role in key industrial technologies that include ironmaking and the combustion and gasification of coal, biomass, and solid waste. Computer models are increasingly used in the design and retrofit of these processes, and the complex design codes require simple and efficient numerical submodels of char combustion. Development of these simple combustion models is made difficult by the complexity of the carbon-oxygen reaction mechanism, whose kinetics are known to be influenced by transient buildup of surface oxides [2-4], the surface migration of these oxides [5], inorganic catalysis [6-8], and pronounced heterogeneity of surface sites, characterized by broad distributions of activation energies both for adsorption [9] and desorption [6,10,11]. These phenomena are difficult to capture in simple combustion models.

A reasonable approach for practical char combustion modeling, therefore, is to postulate semi-global mechanisms that yield kinetic laws with the proper mathematical form to reproduce the major features of the kinetic data, while accepting their inability to predict some minor features, however well established by experiment. Here semi-global kinetics are defined as those comprising more than one explicit reaction step, wherein the steps themselves are not necessarily elementary. Intrinsic kinetics are defined as those not influenced by transport processes. With these definitions, the subject of this chapter is the best choice of semi-global intrinsic kinetic laws for char combustion modeling over the range of technologically important conditions.

A Review of Global Kinetic Parameters from Experiment

A specific goal of this chapter is to identify a semi-global intrinsic kinetic model that can reproduce the correct magnitudes of the temperature dependence (global intrinsic activation energy) and concentration dependence (global intrinsic reaction order) during steady-state combustion across the various temperature ranges of technological interest. The literature on the kinetics of the carbon-oxygen reaction is extensive and there is no universal consensus on the magnitude of the global orders or activation energies. Here a large set of existing data will be reviewed, covering a wide range in temperature and char type, but drawing only from experiments at near atmospheric pressure and reported in the more recent literature — an approach which reveals strong trends in the data.

Figure 4.1 shows a compilation of global intrinsic reaction orders reported in the literature at or near atmospheric pressure. For inclusion in Fig. 4.1 the reported experiments must have included an oxygen partial pressure in the range of 0.1-2 bar, evidence of detailed consideration of transport effects, and a publication date within the last thirty years. The data fall into two categories as reported by the original investigators: (a) Zone I values, corresponding here to all points below 900 K, and (b) intrinsic values extracted from Zone II (here all points above 1100 K) using transport models and/or the classic Thiele mapping relations: $E_{\text{observed}} = 1/2 E$; $n_{\text{observed}} = (n + 1)/2$, where the unsubscripted E and n represent intrinsic values.

Figure 4.1 shows strong evidence for high fractional order (0.6 - 1) in the low-temperature, Zone I regime. Most of these studies employed thermogravimetric analysis, a technique that can be readily assessed for the absence of most forms of transport limitations (through observation of the effects of bed mass and particle size on rate) and allows a nearly direct measurement of reaction order without the added uncertainty of parameter extraction through transport models. An example study in this group is that of Ranish and Walker [1], who, based on simple adsorption/desorption arguments, set out in search of expected zero order behavior at low temperature (733-842 K) and high pressure (1 - 64 bar), but found high order instead.

Results from the Zone II regime are less clear: many authors report half-order apparent kinetics, implying an intrinsic order of zero, but several studies report first order apparent kinetics implying an intrinsic order of unity. A number of authors cited in the Zone II regime report uncertainty in their own value of order (see points in parentheses) and very few have analyzed their data with fractional intrinsic order or with more detailed rate laws [12]. Despite the known difficulties determining accurate kinetic parameters from Zone II data, the set of cited studies as a whole do suggest low intrinsic order at high temperature (> 1100 K). Thus the global order of the carbon-oxygen reaction near atmospheric pressure appears to decrease from high to low as temperature increases from the onset of reaction near 600 K to the beginning of pc-flame conditions at 1500 K. Figure 4.1 shows that this transition occurs in or near some regimes of technological interest, so a kinetic law is sought that will be consistent with this basic trend.

Simple adsorption / desorption arguments strongly suggest the presence of a third regime in the high temperature limit, in which the reaction is adsorption controlled and first order in gaseous oxygen. Essenhigh and Mescher [12] have reported the beginnings of the adsorption control regime in that portion of Monson et al.'s data [13] that lies above 1273 K (with the remainder of the data near the zero order limit). Hong et al. [14] have recently analyzed the same data and found similar results, but report an adequate fit with zero order throughout. Overall, there are insufficient data in Fig. 4.1 to fully define the role of adsorption control at high temperature. It is likely, at atmospheric pressure and above, that the onset of adsorption control occurs in the high temperature regime where the rates are also significantly influenced by boundary layer diffusion, making accurate extraction of the adsorption kinetic parameters challenging in many cases.

A proposed semi-global kinetic law should also be consistent with observed global activation energies. Excluding highly pure heat treated carbons, there is relative agreement about the magnitude of the global intrinsic activation energy; it falls between 105 and 180 kJ / mol with many values in the range 130-150 kJ/mol, especially from the low temperature regime where direct measurement is possible. Other potentially useful

data for model evaluation are curves of reaction rate vs. oxygen partial pressure at a fixed temperature in the Zone I regime. Most studies, however, have not covered a wide range of partial pressures, and yield only a single, local value of the global reaction order as shown in Fig. 4.1. Exceptions are the TGA studies of Suuberg et al. [15], and more recently of Sawaya et al. [16], and of Roberts and Harris [17], both of which were concerned with pressurized combustion. These studies do not find an asymptotic value of the rate as pressure increases, as one might expect from the saturation of surface sites in classical Langmuir-Hinshelwood kinetics; rather the rates continue to increase with increasing pressure, yielding a power-law behavior with $n = 0.64 - 0.7$ [16] or $n = 0.68$ [15]. Roberts and Harris [17] contrast this behavior of O_2 with that of the gasifying agents H_2O and CO_2 , which do show asymptotic behavior in their high pressure data. Suuberg et al. [15] report a fractional reaction order (0.68) that remains constant over two orders of magnitude oxygen partial pressure, and comment that "no presently existing mechanistic model of O_2 gasification of char, with or without porous transport, is likely to be adequate for predicting ... [this behavior]. " The central challenge for the present work is to suggest a kinetic model to reproduce the data in Figure 4.1, the observed magnitudes of the global activation energies, and the CO/CO_2 trends while maintaining simplicity appropriate for flame codes. Three candidate kinetic models are presented in Table 4.1 and discussed in turn below.

Model 1: Global Power-Law Kinetics

Entry 1 in Table 4.1 is the power-law or "nth order" form, which for $n \neq 0$ or 1 is entirely empirical in nature and cannot be derived from simple sequences of elementary steps. This expression is obviously unable to describe the variable global order seen in Fig. 4.1 and is inappropriate as a general form. Over limited ranges of temperature and pressure it may still find practical use, and with $n = 0$ it may be very useful in dedicated pulverized fuel codes that are restricted to the temperature range 1500 - 2000 K, where from Figure 4.1 the reaction appears to be of low order.

Figure 4.1: Compilation of global intrinsic reaction orders reported in the modern literature on char oxidation at near atmospheric pressure. For inclusion in Fig. 4.1 the reported experiments must have included an oxygen partial pressure in the range of 0.1-2 bar, been subject to detailed analysis of kinetics and transport, and been originally reported within the last thirty years. Triangles and circles were points reported as Zone I kinetics; squares are intrinsic parameters extracted from data reported to be in Zone II. Points in parentheses mark where original authors express uncertainty in the accuracy of their own reported reaction orders.

Figure 4.1 Data Key (Reference, carbon form, reaction temperature range)

1. Du et al. [6], soot, 818 K
2. Sorenson and coworkers [32]
 - a,b. bituminous coals, 623-723 K
 - c. sub-bituminous coal, 573-673 K
 - d. coke, 777 - 885 K
 - e. activated carbon, 673-773 K
3. Lin et al. [33], bit. coal, 770 K
4. Suuberg et al. [15], phenol-formaldehyde resin char, 573-673 K
5. Hecker et al. [7] sub-bit. coal, 623 K
6. Ranish and Walker [1], graphite, 733-842 K
7. Croiset et al. [34], bit. coal, 850-1200 K.
8. Smith [35] pet. coke, anthracite, bit. coal, 1200-2270 K
9. Mathies [36], bit. coal, ~1200 K (typical)
10. Monson et al. [13] reanalyzed by Hong et al., [14] and by Essenhigh and Mesher [12]. The latter study reports zeroth order behavior over most of the data, but also the beginnings of a transition to adsorption control at high temperature (see Model 2)
11. Mitchell and McLean [37], pet. coke, coal, 1400-2200 K
12. Smith and Tyler [38], brown coal, 630 - 1812 K
13. Hamor et al. [39], brown coal, 630-2200 K.
14. Kurylko and Essenhigh [40], graphite, 873-1373 K
15. Essenhigh, 1970, anthracite, 1350-1750 K (presented in Essenhigh [19] as reference 37 therein.
16. Field [41], various coals, 1200 - 2000 K
17. Young and Smith [42], pet. coke, 1000 - 1800 K
18. Harris and Smith [43], pet. coke, brown coal, 500-

Model 2: Langmuir-Hinshelwood (Two-Step) Semi-Global Kinetics

Entry 2 in Table 4.1 is the simplest of the Langmuir-Hinshelwood kinetic forms, as has been used for char combustion by a number of researchers. This rate law predicts an effective reaction order that varies with oxygen concentration and temperature. Activation energies for desorption have been measured in the range 160 - 400 kJ/mol [6,11,19], and those for adsorption in the range 10 - 125 kJ/mol [9,19], so for most surface sites $E_{\text{des}} \gg E_{\text{ads}}$. With this inequality the Langmuir-Hinshelwood form exhibits the following two limiting cases at a given pressure: $r_{\text{gas}} = k_2$ (zeroth order, desorption control) in the low temperature limit; and $r_{\text{gas}} = k_1 P_{\text{O}_2}$ (first order, adsorption control) in the high temperature limit. An example of the Langmuir-Hinshelwood behavior is shown in Fig. 4.2 using parameters reported by Essenhigh and Mescher [12] for the high temperature, high-pressure coal char combustion data of Monson et al. [13]. This predicted transition from low to high order with increasing temperature is precisely the opposite of the experimental behavior in the low-to-intermediate temperature range of Figs. 4.1 and 4.2. This discrepancy is further illustrated in the recent work of Hong et al. [14], who applied the Langmuir-Hinshelwood rate equation to three data sets from the literature. For two data sets in the high temperature regime they report the best fits with strict zero order (desorption control), in agreement with the general trend in Fig. 4.1 and 4.2 data. For the data of Ranish and Walker [1] at low temperatures (733 - 813 K) they achieve the best fits with $E_{\text{des}} = 172$ kJ/mol and $E_{\text{ads}} = 214$ kJ/mol [14]. These inverted activation energies ($E_{\text{ads}} > E_{\text{des}}$) were necessary to describe the observed decrease in reaction order with increasing temperature. The Langmuir-Hinshelwood law fit the data successfully, but the inverted activation energies likely negate any mechanistic

Table 4.1
Global and Semi-Global Mechanisms[†](left) and Rate Laws (right)

<i>Model 1. Global power-law</i> 1. $C + O_2 \rightarrow CO / CO_2$	$r_{\text{gas}} = k P_{O_2}^n$
<i>Model 2. Langmuir-Hinshelwood</i> 1. $C + O_2 \rightarrow C(O)$ 2. $C(O) \rightarrow CO$	$r_{\text{gas}} = \frac{k_1 k_2 P_{O_2}}{k_1 P_{O_2} + k_2}$ (non-dissociative form)
<i>Model 3. Three-step semi-global</i> 1. $C + O_2 \rightarrow 2C(O)$ 2. $C(O) + O_2 \rightarrow CO_2 + C(O)$ 3. $C(O) \rightarrow CO$	$r_{\text{gas}} = \frac{k_1 k_2 P_{O_2}^2 + k_1 k_3 P_{O_2}}{k_1 P_{O_2} + k_3/2}$ $CO/CO_2 = \frac{k_3}{k_2 P_{O_2}}$ <p><i>all Model 3 calculations use:</i></p> $A_2 = 5.7 \cdot 10^{-4} \text{ bar}^{-1}$ $E_2 = 130 \text{ kJ/mol}$ $E_3 = 180 \text{ kJ/mol}$ (normalized by $A_3 = 1.0$)
[†] in these semi-global "mechanisms", no attempt is made to define the precise stoichiometry of the steps or complexes, and the simplest forms of the rate laws are used, in which the reactions are assumed to be all first order (rather than second order) in surface densities.	

significance of the fit. Langmuir-Hinshelwood kinetics are also unable to describe the persistent nth order behavior seen by Sawaya et al.[16] over a factor of 50 in P_{O_2} , and by Suuberg et al. [15] over a factor of 100 in P_{O_2} . The mathematical form of the Langmuir-Hinshelwood law allows zero order or first order as limiting cases, as well as a transition zone between the two, but the transition zone spans only about one order of magnitude in P_{O_2} . The simplest LH law is thus inappropriate as a general form, although it can be very useful in certain ranges of temperature and oxygen concentration.

Model 3: Three-Step Semi-Global Kinetics

Both power-law and Langmuir-Hinshelwood kinetics do not provide even the crudest description of the reaction order data in Figs. 4.1 and 4.2. A solution to this problem is suggested by recent work on reactions involving gas phase oxygen with surface complexes:

which may or may not also involve the generation of a new complex, C(O), on the product side. Reactions of this class have been observed in a number of more recent studies [3,10,11,21], with the most direct proof coming from observations of isotopically mixed carbon dioxide, C¹⁸O¹⁶O, as the product of transient kinetic studies employing rapid switch-over from ¹⁸O₂ to ¹⁶O₂ [10,11,21]. This provides direct evidence for reaction of gas-phase oxygen, ¹⁶O₂, with previously formed complex, C(¹⁸O). In terms of magnitude, Ahmed and Back [3] find O₂- complex reactions to be an important source of CO₂ for gasification in oxygen pressures above 1 Torr; Zhuang et al. [10] find this reaction type to be the *main route* for CO₂ formation at 773 K in 0.05 bar O₂ using isotopic tracers. Most recently, Haynes and Newbury [11] report from isotopic tracer studies that 45% of the gasification at 873 K is due to O₂-complex reactions, falling to only 5% of the gasification at 1073 K. Further, both Zhuang et al. [21] and Haynes and Newbury [11] find that the O₂-complex reaction proceeds even on the thermally stable complexes, which in the absence of O₂ would not turn over fast enough at the reaction temperature to contribute significantly to the observed gasification. Thus in the presence of a broad distribution of desorption activation energies, the most stable complexes turnover preferentially by oxyreactivity (Eq.1), while on the same surface the labile complexes turnover preferentially by thermal desorption, producing a mixed reaction mode [11]. Analogous gas-complex reaction steps have been postulated to explain the kinetics of gasification with CO₂ [22] and steam [23].

These detailed surface studies provide a promising explanation for the high reaction orders at low temperature, since reaction (1) is nominally first order in oxygen. The following semi-global mechanism for steady-state combustion is suggested:

which is the basis for Model 3 in Table 4.1. It is in essence a version of the qualitative mechanistic pathway proposed by Tomita and coworkers [10], reduced here to allow quantitative treatment in combustion modeling.

In this semi-global "mechanism," any of the steps may be a lumped description of several more elementary steps. In particular, step 2 may represent any of the following:

- (a) direct collisional interaction between gaseous oxygen and a surface complex. This is a true Eley-Rideal reaction [24] as postulated early by Langmuir [25,26] for CO and H₂ reactions with oxygen complexes on platinum, and later generalized by Rideal [27].
- (b) the attack of sites adjacent to an existing complex resulting in complex destabilization and rapid desorption of CO₂. The rapid desorption makes this process first order in molecular oxygen.
- (c) Some modes of induced or intrinsic heterogeneity [1,28], in which adsorption activation energy increases and desorption activation energy decreases with increasing coverage. This trend can lead to partial or complete adsorption control at low temperatures where fractional coverage is very high.

Step 2 in Eq. 2 is the most appropriate semi-global step to describe elementary mechanisms (a) or (b). Mechanism (c) is better described by explicit models of surface heterogeneity, but step 2 in Eq. 2 can still mimic its global behavior, at least crudely, as it is a first-order process in gaseous oxygen that also requires the presence of complex. A number of observations support step 2 above as the primary pathway to CO₂, rather than

Figure 4.2. Data from Fig. 4.1 compared to behavior of two semi-global models. Model 2: Langmuir-Hinshelwood rate law (see 10 in key) at two different oxygen partial pressures; and Model 3: three-step semi-global rate law at 1 bar. The local global order is calculated from these models as: $n = (\text{dlnR} / \text{dlnP})_T$.

Model 2 parameters: $A_{\text{ads}} = 0.435$, $E_{\text{ads}} = 31.4$ kJ/mol, $A_{\text{des}} = 4.5$, $E_{\text{des}} = 100$ kJ/mol from Klimesh and Essenhigh [20].

Model 3 parameters: $A_2 = 5.7 \cdot 10^{-4}$, $E_2 = 130$ kJ/mol, $E_3 = 180$ kJ/mol (normalized by $A_3 = 1.0$). Dashed line: fast (non-controlling) adsorption. Solid line: possible beginnings of adsorption control, using $A_1 = 3.3 \cdot 10^{-4}$, $E_1 = 35$ kJ/mol.

which is the favored explanation for CO₂ formation in all but the most recent literature. These observations include the high CO/CO₂ ratios seen during vacuum TPD relative to gasification conditions [1,6,21,29], the recent quantification of C¹⁸O¹⁶O in isotope tracer studies [10,11,21], and the inability of Eq. 3 to predict high reaction order at low temperature without additional model complexity as pointed out in this study.

For the quantitative treatment of Model 3 (Eq. 2), we will not define the precise stoichiometry with respect to free surface sites, "C" and will adopt instead the simplest form of the corresponding rate laws, which assume first order in site density:

$$R_1 = k_1 P_{O_2} (1-\theta) \quad (4)$$

$$R_2 = k_2 P_{O_2} \theta \quad (5)$$

$$R_3 = k_3 \theta \quad (6)$$

where θ represents the fraction of sites occupied by complex. These laws can be combined to yield the steady state expression for overall gasification rate and primary CO/CO₂ ratio:

$$r_{\text{gas}} = \frac{k_1 k_2 P_{O_2}^2 + k_1 k_3 P_{O_2}}{k_1 P_{O_2} + k_3/2} \quad (7)$$

$$\text{CO} / \text{CO}_2 = \frac{k_3}{k_2 P_{O_2}} \quad (8)$$

Based on the results of Haynes and Newbury [11] and the arguments of Ahmed and Back [3], one expects $E_3 > E_2 > E_1$, which yields the following limiting cases:

$$\text{A) low temperature:} \quad r_{\text{gas}} = k_2 P_{O_2} \quad (\text{O}_2\text{-complex reaction control}) \quad (9)$$

(k_3 small)

$$\text{B) very high temperature:} \quad r_{\text{gas}} = 2 k_1 P_{O_2} \quad (\text{adsorption control}) \quad (10)$$

(k_3 large)

both first-order processes. Depending on the magnitudes of the rate constants, several other degenerate forms may be seen at intermediate temperatures, including:

$$\text{C) low-moderate temperature: } r_{\text{gas}} = k_2 P_{\text{O}_2} + k_3 \quad (\text{mixed desorption / O}_2 \text{ / complex control}) \quad (11)$$

$$(k_1 P_{\text{O}_2} \gg k_3)$$

$$\text{D) moderate temperature } r_{\text{gas}} = k_3 \quad (\text{desorption control}) \quad (12)$$

$$(k_1 P_{\text{O}_2} \gg k_3 \gg k_2 P_{\text{O}_2})$$

$$\text{E) high-moderate temperature: } r_{\text{gas}} = \frac{k_1 k_3 P_{\text{O}_2}}{k_1 P_{\text{O}_2} + k_3/2} \quad (\text{Langmuir-Hinshel. type mixed adsorption / desorption control}) \quad (13)$$

$$(k_1 P_{\text{O}_2}, k_3 \gg k_2 P_{\text{O}_2})$$

It is immediately seen that inclusion of step 2 in Eq. 2 creates the potential to describe the data in Figs. 4.1 and 4.2 — as temperature increases global reaction order can shift from high (O₂-complex control, "A") to low (desorption control, "D") and back to high again (adsorption control "B"). It also provides some information on the CO/CO₂ ratio in the primary products which can be independently tested against data.

The full rate law, Eq. 7, contains 6 kinetic constants: the three pre-exponential factors, A₁, A₂, A₃; and activation energies: E₁, E₂, E₃ that define the three rate constants in Eq. 7, but not all need to be adjusted freely to test against the data. First, the experimental evidence for high temperature adsorption control is not perfectly clear in Figs. 4.1 and 4.2, so no attempt was made to adjust A₁ and E₁, as they affect only the high temperature region. Figure 4.2 shows two curves for the Model 3 prediction, a dashed curve in which A₁ and E₁ were set to give fast (non-limiting) adsorption, and a solid curve in which E₁ was set to a typical value for adsorption (35 kJ/mol) [19] and A₁ adjusted to show the beginnings of adsorption control at the highest temperatures in Fig. 4.2 — indicated by the upturn of the order curve. In addition, there was no attempt to predict an absolute rate, only the global order, and this is sensitive to the ratio A₂/A₃, but not to A₂ or A₃ individually. Therefore A₃ was set to unity and 3 parameters were adjusted: A₂, E₂, E₃ to closely match three sets of observations: (1) the global reaction order at atmospheric pressure (Fig. 4.2), (2) measured CO/CO₂ ratios surveyed by Skokova [18] (Fig. 4.3), and (3) the characteristic values of the global activation energy for oxidation, 105-180 kJ/mol.

A reasonable description of all the global behavior ratio is achieved with the following kinetic constants:

$$A_2 = 5.7 \cdot 10^{-4} \text{ bar}^{-1}, \quad E_2 = 130 \text{ kJ/mol}; \quad E_3 = 180 \text{ kJ/mol}$$

all normalized by setting $A_3 = 1.0$. Model 3 with these parameters provides an adequate fit to the global order data (Fig. 4.2), typical CO/CO₂ ratio behavior (Fig. 4.3), and gives an activation energy (Fig. 4.4) that varies from about 130 kJ/mol at $T = 700 \text{ K}$ to 180 kJ/mol at T from 900 - 1700 K. The slight increase in activation energy between 700 K and 900 K may or may not be detectable in laboratory data (as appreciated by visual examination of Fig. 4.4) or may be easily overridden by secondary effects not described by such a simple, semi-global model.

To achieve the fits in Figs. 4.1-3, $E_3 > E_2 > E_1$, as expected. Further, E_1 and E_3 are in the range quoted for adsorption and desorption activation energies [9,12], while E_2 is intermediate as expected, although it is much larger than the single value in the literature (130 kJ/mol vs. 34 kJ/mol estimated by Haynes and Newbury [11]). The effective "activation energy" for the CO/CO₂ ratio by Model 3 is $E_3 - E_2$ or 50 kJ/mol, very similar to the value reported by Arthur (52 kJ/mol) and in the middle of the range of later data sets (25-75 kJ/mol) as reviewed by Skokova [18].

The behavior of Model 3 can also be compared to the observation by Suuberg et al. [15] and Sawaya et al. [16], and Roberts and Harris [17] that the rate of low temperature oxidation does not reach an asymptotic value at high O₂ partial pressures, as would be expected from the saturation of surface sites by classical Langmuir-Hinshelwood kinetics. Figure 4.5 shows the predicted oxygen pressure dependence at 900 K using the full Model 3 mechanism with the standard parameter set (in Table 4.1). Clearly no saturation behavior is observed at high pressures. Figure 4.5 also shows a power-law fit with $n=0.8$. Model 3 cannot be strictly reduced to a power-law form, but can be approximated by one over about 1.5 orders of magnitude in oxygen partial pressure (1-30 bar). With two

orders of magnitude variation in P_{O_2} , the deviation from the power law behavior becomes quite clear, and therefore Model 3 alone cannot quite explain Suuberg's observation of persistent n th order behavior over two decades in P_{O_2} [15].

Figure 4.3. Survey of measured CO/CO_2 ratios adapted from Skokova [18] compared to predictions of the three-step, semi-global model (Model 3) with parameter set from Table 4.1: $A_2 = 5.7 \cdot 10^{-4} \text{ bar}^{-1}$; $E_2 = 130 \text{ kJ/mol}$; $E_3 = 180 \text{ kJ/mol}$ (all normalized to $A_3 = 1.0$). The shaded region encompasses about 80% of the data points in the original Skokova diagram [18]. Also shown is the correlation describing the CO/CO_2 measurements of Arthur [44].

Finally, Model 3 offers a simpler explanation than that previously available [1] for reaction orders that decrease with increasing temperature. The critical element in Model 3 is the inclusion of the CO_2 -producing step, step 2, which gives high order behavior at low temperature and near atmospheric pressure. It is likely that the role of reaction 2 (in Eq. 2) has been underestimated in much of the previous literature due to its diminished importance relative to Eq. 3 at the very low pressures used in many fundamental surface studies. This point has also been made by Ahmed and Back [3], who claim reaction 2 (in Eq. 2) is important in their data above $10^{-3} \text{ bar } O_2$, in contrast to the conclusions reached in previous studies at 10^{-6} bar [45,46]. By the argument of Ahmed and Back [3] it would certainly be dominant at the near atmospheric pressures in Figs. 4.1 and 4.2.

Model 3 for its extreme simplicity does a remarkable job of describing the trends in global reaction order, CO/CO₂, and global activation energy. It is not capable, however, of describing a number of other known features of the carbon-oxygen [47], for which more detailed models are still needed.

Figure 4.4. Points show Arrhenius behavior of Model 3 with parameter set: $A_2 = 5.7 \cdot 10^{-4}$ bar⁻¹; $E_2 = 130$ kJ/mol; $E_3 = 180$ kJ/mol (all normalized to $A_3 = 1.0$). For illustration the calculation also uses $A_1 = 3.3 \cdot 10^{-4}$ bar⁻¹; $E_1 = 35$ kJ/mol to show the beginnings of a transition to adsorption control at high temperature. The lines point out two limiting regimes in the model.

Figure 4.5. Model 3 behavior as a function of oxygen partial pressure at 900 K. The model behavior can be approximated as n th order with $n = 0.8$ over about 1.5 decades of oxygen partial pressure. Model 3 parameters are as in Figs. 4.2, 4.3, and 4.4.

Chapter 4 Conclusions

1. For char oxidation at O_2 partial pressures near atmospheric, there is strong experimental evidence for high intrinsic order in the low temperature, Zone I regime ($< 900\text{ K}$), significant though much weaker evidence for low intrinsic order in the high temperature, Zone II regime ($> 1200\text{ K}$), and some suggestion of a transition toward a second higher-order regime at very high temperature ($> \text{about } 1600\text{ K}$).
2. Neither power-law kinetics nor Langmuir-Hinshelwood kinetics are appropriate as general forms for describing char combustion kinetics over the entire range of technological interest in temperature and oxygen pressure. Both zeroth order and Langmuir-Hinshelwood treatments can be appropriate under restricted conditions, especially at the high-temperatures prevailing in pulverized fuel combustion.
3. A three-step semi-global mechanism incorporating O_2 -complex reaction is capable of describing the basic trends in global order, global activation energy, and CO/CO_2 ratio over a wide range of combustion conditions. The corresponding rate law is promising as a semi-empirical form for use in diverse combustion applications.
4. Beyond the global trends, there are many known features of carbon-oxygen kinetics that cannot be easily captured by models of the semi-global variety, and these features may be closely tied to heterogeneity in the energetics and chemical functionality of specific carbon active sites and their oxides.

Chapter 4 References

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CHAPTER 5

ON THE ORIGIN OF POWER-LAW KINETICS IN CHAR COMBUSTION

A limitation of the semi-global rate model presented in the previous chapter is its inability to describe the persistent power-law behavior typically observed in low-temperature char combustion. This chapter focuses on the origin of the power law behavior and also serves as a comparative evaluation of the straight power law approach (used in CBK8), relative to more complex rate laws such as that used in CBK/E. The overall goal, again, is to identify the best approach for high pressure conditions expected in advanced combustors and gasifiers.

The simple stoichiometry of the carbon/oxygen reaction, $C + O_2 \rightarrow CO / CO_2$, belies a complex kinetic behavior, which has to date prevented a consensus on the kinetic parameters or even the proper form of the rate expression. Identifying the most appropriate rate form remains an important practical goal, since in the long term it will allow more meaningful correlation and unification of the data needed to design furnaces and burner systems.

This chapter focuses initially on low-temperature studies (< 1000 K) where the kinetic data are much more suitable to detailed analysis, and on near-atmospheric studies ($P_{ox} > 0.01$ bar), which are of greatest technological relevance. This literature contains many reports of fractional orders (see Fig. 5.1), a fact that suggests complex kinetics. The Fig. 5.1 data includes a large and significant cluster of high fractional reaction orders, but also credible reports of low order [1,2], and a robust kinetic law must be capable of predicting both. Most of the studies in Fig. 5.1 employ relatively narrow ranges of oxygen pressure (factors of 3-10) and the reported orders that are best interpreted as local values, $n_{loc} = d \ln R / d \ln P$, that are slopes of some governing kinetic law whose functional form is not directly revealed. One of several exceptions in the literature is the study of Suuberg et al.[5.4], who measured combustion rates from 0.005 - 1 bar oxygen partial pressure from 573-673 K for a phenol-formaldehyde resin char (see Fig. 5.2). These authors find that the rates followed a power-law form: $R = k P_{ox}^n$, where n is constant at 0.62 over the entire range of oxygen pressure (see Fig. 5.2a). Similar

behavior has been observed in a recent study motivated by technological interest in high-pressure combustion and gasification[5,6] (see Fig. 5.2b).

This "persistent" power-law behavior is inconsistent with simple theories of adsorption and desorption on homogeneous (i.e. single site type) surfaces, which give the Langmuir law:

$$R = k_{des} k_{ads} P_{ox} / (k_{des} + k_{ads} P_{ox}) \quad (1)$$

This form requires the reaction to be first order, zeroth order, or in a transition zone between the two. Logarithmic differentiation of Eq. 1 yields the local reaction order implicit in the Langmuir law:

$$n_{local} = d \ln R / d \ln P = 1 / [1 + (k_{ads} P_{ox} / k_{des})] \quad (2)$$

Defining the transition region as $0.2 < n_{local} < 0.8$, its width by Eq. 2 is always a factor of 16 in oxygen pressure regardless of the specific values of k_{ads} and k_{des} . Experimental

Figure 5.1. Summary of measured reaction orders reported in the literature for carbon oxidation at $T < 1000$ K, $P_{ox} > 0.01$ bar. **A:** graphitic carbons, **B:** non-graphitic carbons. The coal char data in this figure was taken from a previous compilation [3].

verification of this transition is conspicuously absent in the low-temperature carbon oxidation literature. The power law behavior reported by Suuberg et al. [4] over a factor of 200 in oxygen pressure is particularly incompatible with the simple Langmuir form (see Fig. 5.2). Further since measured activation energies for transient desorption are typically much greater than those for adsorption, this form requires zeroth order in the low-temperature, high-pressure limit, which is incompatible with the majority of the low-temperature data in Fig. 5.1. The power-law form may be an attractive alternative, but without a fundamental basis its use in combustion models will remain empirical and ultimately controversial.

The present chapter addresses the mechanistic origin of power-law kinetics by drawing from the fundamental literature on heterogeneous (real) surfaces. We will show that global power-law kinetics is a natural consequence of the already well-established heterogeneity of real carbon surfaces [7-10], whether the heterogeneity is intrinsic or induced. The chapter then compares the specific heterogeneous surface model of Haynes[11] to several example datasets and the results used to discuss the main features of the carbon oxidation database in the intrinsic regime at $T < 1000$ K and $P_{ox} > 0.01$ bar.

Simple Treatments of Turnover Kinetics on Heterogeneous Surfaces

This section explores the effects of surface heterogeneity on the global kinetics of a general heterogeneous reaction using simple theories of intrinsic and induced heterogeneity.

Intrinsic heterogeneity

Almost all solid surfaces exhibit site-to-site variations in turnover rates that reflect intrinsic local variations in bonding, composition, or surface nanotopology[12]. This intrinsic heterogeneity appears most notably as variations in activation energies for adsorption, surface reaction, and/or desorption. The simplest model of intrinsic heterogeneity assumes Langmuir kinetics on parallel, independent reaction sites with a

Figure 5.2. Global pressure dependence of low-temperature carbon oxidation kinetics on non-graphitic chars in the data of **A**: Suuberg et al. [4] for a phenol-formaldehyde resin char, and **B**: Madsen et al.[5] (see also Hecker et al.[6]) for high pressure oxidation of Pittsburgh seam bituminous coal char at various temperatures (triangles: 823 K, circles: 773, diamonds: 748K, squares: 723 K). The straight lines are empirical power-law fits with the best-fit exponent for each curve shown on the graph. The dashed curve shows the single-site Langmuir form, which always undergoes a transition from global first to zeroth order over a factor of 16 in oxygen pressure.

distribution of activation energies. For illustration we consider the effect of a distribution of the desorption energies only, and write the total rate as:

$$R_{global} = \int f(E_{des}) R(E_{des}) dE_{des} \quad (3)$$

where R_{global} is the overall rate of gasification, $f(E_{des})$ is the site density distribution, and R is given by Eq. 1 where k_{des} depends on E_{des} , and k_{ads} is a simple rate constant. Figure 5.3 shows the pressure dependence predicted by Eq. 3 for Gaussian distributions of E_{des} with various values of the standard deviation, σ_{E-des} . As the distribution breadth, σ_{E-des} , increases from 0 (the uniform surface) to 80 kJ/mol, the pressure dependence shifts gradually from the Langmuir-type to a linear $\log R_{global}$ - $\log P$ relation. At $\sigma_{E-des} = 20$

kJ/mol the R_{global} - P relation is adequately approximated by a power law function over about 3 orders of magnitude in pressure, while at $\Delta E_{des} = 80$ kJ/mol the behavior is indistinguishable from power law kinetics over the entire range of calculation. Whether power-law behavior is observed in practice depends critically on the breadth of the energy distribution, ΔE_{des} for the solid surface in question.

Figure 5.3. Behavior of the global reaction rate predicted by simple treatment of generic solid surfaces possessing *intrinsic* site heterogeneity. As the breadth of the desorption activation energy distribution, ΔE_{des} , increases, the global behavior gradually shifts from Langmuirian kinetics with its surface-saturated asymptote to a linear $\log R_{global}$ vs. $\log P$ relationship indicating power-law kinetics.

Induced heterogeneity

A second form of surface heterogeneity is not intrinsic to the solid phase, but occurs when adsorbed species influence the energetics of surface reactions. Chemisorbed species can alter solid surface properties through electron donation or withdrawal, or can interact with neighboring adsorbed species in either a cooperative or competitive fashion.

Chemisorption on one site can either inhibit adsorption on neighboring sites by steric exclusion or can enhance adsorption on those sites by adsorbate-adsorbate attractive forces[12]. In each case the result is an activation energy for adsorption and/or desorption that varies with surface coverage, θ .

A very simple model describing this induced heterogeneity allows both adsorption and desorption activation energies to vary with coverage according to:

$$E_{ads} = E_{ads}^o + \alpha \theta ; \quad E_{des} = E_{des}^o - \beta \theta \quad (4)$$

where α and β are parameters. Equating the rates of adsorption and desorption at steady state yields:

$$R_{global} = A_{ads} e^{-(E_{o,ads} + \alpha \theta / RT)} P_{ox} (1 - \theta) = A_{des} e^{-(E_{o,des} - \beta \theta / RT)} \theta \quad (5)$$

which defines a complete model that for a given set of conditions can be solved numerically for coverage, θ and then global rate. At $\alpha = \beta = 0$ this model reduces to the one-site Langmuir form, while Fig. 5.4 shows that large values of α and/or β give a global behavior that is essentially indistinguishable from power-law kinetics. The global behavior is quite similar to that for intrinsic heterogeneity in Fig. 5.3, though the mathematical formulations are rather different, Eq. 3 being a statistical relation.

The origin of this power-law behavior imbedded in Eq. 5 can be understood as follows. Adsorption slows sharply as coverage increases, and desorption slows sharply as coverage decreases, so the steady-state coverage, which represents a competition between adsorption and desorption rates, does not easily reach either limiting case (desorption control at $\theta = 1$, or adsorption control at $\theta = 0$). Rather, the coverage remains at intermediate values over wide ranges of pressure, and the reaction occurs in a stable regime of mixed adsorption/desorption control that yields n^{th} -order kinetics.

Figure 5.4.

Behavior of the global reaction rate predicted by simple treatment of generic solid surfaces possessing *induced* heterogeneity. Parameters ΔH_a , ΔH_d describe the coverage-dependence of adsorption and desorption activities energies respectively. As they increase, the global behavior gradually shifts from Langmuirian kinetics to a linear $\log R_{\text{global}}$ vs. $\log P$ relationship indicating power-law kinetics.

Surface Heterogeneity in Carbon Oxidation

The turnover model of Haynes

Here we consider a specific formulation for carbon oxidation that has been developed by Haynes and coworkers[10,13] from transient measurements of adsorption and desorption for Spherocharb. This work culminated recently in a turnover model[11] based on the following reaction sequence:

1. $\text{C} + \text{O}_2 \rightarrow \text{C(O)} + \text{CO}$
2. $\text{C(O)} \rightarrow \text{CO}$ (6)
3. $\text{C(O)} + \text{O}_2 \rightarrow \text{C(O)} + \text{CO/CO}_2$

The Haynes turnover model contains explicit descriptions of site heterogeneity and has been shown to provide a good prediction of Spherocharb burning rates at 2.7 Pa from 873-1073 K[11]. Here we use a pseudo-steady version of this model to explore carbon

oxidation kinetic behavior over wide pressure ranges. The key equations in the Haynes turnover model used here are:

$$R_{ads} = A_{ads} e^{(-E_{ads}/RT)} P_{ox} (1-\theta) \quad (7)$$

where θ is the fraction coverage and A_{ads} comes from gas kinetic theory as:

$$A_{ads} = S / (2\theta M_{O_2} RT)^{1/2} \quad (8)$$

The activation energy, E_{ads} , is coverage-dependent according to

$$E_{ads} = a + b \ln(N) \quad (9)$$

where N is the total number of oxides and a and b are parameters. Experimentally determined parameters for Spherocharb are: $a = 165$ and $b = 10.38$ for N in mol/kg-carbon and E_{ads} in kJ/mol [11]. The desorption rate is obtained by integration over a distribution of sites of varying desorption activation energy:

$$R_{des} = \int A_{des} e^{(-E_{des}/RT)} q(E_{des}) f(E_{des}) dE_{des} \quad (10)$$

where A_{des} is 10^{14} sec^{-1} and the site density $f(E_{des})$ distribution has been determined for Spherocharb by TPD experiments with variable isothermal soak time. The present version adopts a Gaussian form for the distribution, as also assumed in the work of Du et al.[8], with baseline parameters from the Spherocharb studies: mean $E_{des} = 300 \text{ kJ/mol}$ and $\sigma_{des} = 60 \text{ kJ/mol}$.

At pseudo-steady-state, $R_{ads} = R_{des}$ since the gas-complex reaction step propagates the complex, and the overall gasification rate is:

$$R_{global} = R_{des} + R_{g-c} \quad (11)$$

The gas/complex reaction step underlying R_{g-c} (step 3) is not as well understood as steps 1 and 2. There is evidence of its importance at 2.7 Pa and 870-1080 K, but a reliable assessment of its role in traditional char combustion kinetic experiments at and above atmospheric pressure awaits further experimental data. The present study therefore focuses on the role of heterogeneity in reaction steps 1 and 2, where detailed quantitative treatments of site energy distributions are available from TPD experiments[10]. A minor modification was made to the original Haynes formulation[11] by introducing a total site number as a parameter to facilitate the examination of widely diverse carbon surfaces. A value of 0.85 mol/gm was used for the disordered carbons in this study (a value near the maximum experimental coverage in transient chemisorption data for Spherocarb[11]), while for graphite the parameter was adjusted to fit the data of Tyler as described later.

Figure 5.5 shows the Haynes model predictions with the previously determined numerical values for Spherocarb. The steady-state global kinetics follow fractional power-law kinetics ($n = 0.78$) over the entire numerical range — at least 6 orders of magnitude in oxygen pressure. In agreement with the previous simple heterogeneous surface model, this model of carbon oxidation predicts persistent n^{th} -order behavior to be a natural consequence of a broad distribution of activation energies. Figure 5.5 also shows a series of cases in which the E_a distribution for desorption is artificially narrowed in steps to examine behavior. At half the original breadth ($\Delta = 30$ kJ/mol) the persistent n^{th} -order behavior remains, but when the heterogeneity is essentially removed ($\Delta = 0.1$ kJ/mol), curvature in the $\log R_{\text{global}} - \log P_{\text{ox}}$ space appears. Only when both the desorption and adsorption heterogeneity are effectively removed ($\Delta = 0.1$ kJ/mol, $b = 0$ in Eq. 9) does the model collapse to the simple Langmuir law with its distinct transition from first to zeroth order. The actual distribution breadth for Spherocarb is 60 kJ/mol, and a similar TPD profile has been reported for a low-rank coal char[14], so based on these results persistent power-law behavior would be expected for both of these disordered carbons.

Partitioning of $f(E_{des})$ into three site classes

Figure 5.6 provides more insight into the origin of the persistent power-law behavior. For each value of E_{des} in the distribution, adsorption and desorption rates can be equated and the resulting local value of coverage, $\bar{\theta}(E_{des})$, can be used to define three site classes:

Figure 5.5. Oxygen pressure dependence predicted by a pseudo-steady version of the Haynes turnover model[11]. Using the original reported parameters for Spherocharb ($E_{des} = 60$ kJ/mol) the predictions follow a global power-law form ($n=0.78$) over at least 6 orders of magnitude in oxygen pressure. Additional curves give predictions with the original breadth of the desorption activation energy distribution artificially reduced from 60 to 30 to 0.1 kJ/mol. Note the mean desorption activation energy was adjusted to hold the absolute rate fixed at an oxygen pressure of 0.1 bar. The black squares show the Langmuirian behavior only when both adsorption and desorption distributions are narrowed to effectively zero breadth.

adsorption limited sites with $\bar{\theta} \ll 1$, desorption-limited sites with $\bar{\theta} \gg 1$, and transitional sites with fractional coverage. For this analytical form we define a parameter $E_{0.5}$ as the

desorption activation energy on those sites that are exactly half covered ($\theta=0.5$) at pseudo-steady-state, obtained by solving:

$$A_{ads} e^{(-E_{ads}/RT)} P_{ox} (1-\theta) = A_{des} e^{(-E_{des}/RT)} \theta \quad (12)$$

Figure 5.6. Distribution of desorption activation energies originally reported for Sphero carb [11]. The distribution curve is labeled to show the various site populations for an example set of conditions (873 K, 0.1 bar O_2). Under these conditions the sites with 50% coverage have desorption activation energies of 253 kJ/mol ($E_{0.5} = 253$ kJ/mol). The top panel shows coverage, θ , as a function of E_{des} .

for E_{des} when θ is 0.5 (see Fig. 5.6). It can be shown that θ goes from 0.1 to 0.9 over $\Delta E = 4.4RT$ or so the transition zone is conservatively defined as $E_{0.5} \pm 3RT$. The contribution to steady gasification from all sites with E above $E_{0.5} + 3RT$ is negligible, and these constitute the abundant stable oxides observed during low-temperature gasification experiments.

The global gasification reaction is thus dominated by two contributions: a first-order contribution on the bare sites in the low- E_{des} tail and a zeroth order contribution on covered sites that is attenuated rapidly as E_{des} increases due to rapidly decreasing reactivity as the stable oxide regime is approached and entered. In practice the fraction of these covered sites that significantly contributes is often small and the result is high fractional order, as observed experimentally (Fig. 5.1). Finally, since the threshold value, $E_{0.5}$, changes only slowly with oxygen pressure, this physical picture remains unaltered over wide pressure ranges, and persistent fractional order is observed, again in agreement with experiments (Fig. 5.2).

Derivation of an approximate analytical expression for n_{global}

Since the stable oxide does not turn over at a significant rate, there are two components to steady gasification: (1) first-order adsorption-limited reaction on bare sites with $E < E_{0.5} - 3RT$, and (2) mixed-order reaction on partially covered sites in the transition zone: $E_{0.5} - 3RT < E < E_{0.5} + 3RT$. In the limit of large ΔE_{des} , the transition zone becomes small relative to the total distribution breadth and can be adequately described as a step function in coverage from 0 to 1 at the threshold value of $E_{0.5}$. This overestimates the rate in the transition zone for both site types, but the errors approximately cancel when the expression is differentiated for reaction order, whose value depends largely on the relative contribution of the two site types to the overall rate. In this limit there are only bare sites ($E < E_{0.5}$) and covered sites ($E > E_{0.5}$) yielding the following two contributions to the overall rate:

$$R_l = A_{ads} e^{(-E_{ads}/RT)} P_{ox} \int_0^{E_{0.5}} f(E_{des}) dE_{des} \quad (13)$$

$$R_0 = \int_{E_{0.5}} f(E_{des}) A_{des} e^{(-E_{des}/RT)} dE_{des} \quad (14)$$

where R_1 is the first-order component on bare sites and R_0 the zeroth order component on the covered sites and the global rate is

$$R_{global} = R_1 + R_0 \quad (15)$$

Differentiation of Eq. 15 together with Eqs. 13, 14 yields, after some algebraic manipulation,

$$\frac{d \ln R_{global}}{d \ln P_{ox}} \equiv n_{global} = \frac{R_1}{R_1 + R_0} + \frac{R_0}{R_1 + R_0} \left[\frac{P_{ox}}{RT} \right] \frac{dE_{ads}}{dP_{ox}} \quad (16)$$

The second term containing dE_{ads}/dP_{ox} is difficult to simplify but is small under most practical conditions. Ignoring this term, Eqs. 13, 14, and 16 can be taken together give a working relation for the reaction order. This relation can be greatly simplified by recognizing that the local desorption rate: $A_{des} e^{(-E_{des}/RT)}$ is equal to the local adsorption rate, $A_{ads} e^{(-E_{ads}/RT)} P_{ox}$, at $E_{0.5}$, yielding:

$$n_{global} \approx \frac{1}{1 + (1/A_{<0.5}) \int_{E_{0.5}} f(E_{des}) e^{((E_{0.5} - E_{des})/RT)} dE_{des}} \quad (17)$$

Where $A_{<0.5}$ is the area of the E_{des} distribution below $E_{0.5}$. An even simpler form can be written for very broad distributions where $f(E_{des})$ changes slowly compared to $e^{((E_{0.5} - E_{des})/RT)}$. In this case $f(E_{des})$ is approximated as $f(E_{0.5})$ and simple integration yields

$$n_{global} \approx \frac{1}{1 + RTf(E_{0.5})/A_{<0.5}} \quad (18)$$

where $f(E_{0.5})$ is the height of the distribution at $E_{0.5}$. For the parameters used to generate Fig. 5.6: $f(E_{0.5}) = 0.0065$ mol/kJ, $A_{<0.5} = 0.22$, $T = 873$ K, and Eq. 18 yields $n_{global} = 0.82$ in

good agreement with Eq. 17 ($n_{global} = 0.81$) and in reasonable agreement with the full theory ($n_{global} = 0.78$), which requires numerical solution of Eqs. 7-10 and fitting of the resultant $R_{global} - P_{ox}$ relation with a power law expression.

Application to the Carbon Oxidation Database at $T < 1000$ K, $P > 0.01$ Bar

The previous sections demonstrate that surface heterogeneity, whether intrinsic or induced, is capable of explaining the long-standing paradox of power-law kinetics in carbon oxidation. The particular formulation of Haynes[11] is a promising candidate for application to the carbon oxidation database, but the model requires extensive surface characterization, which to date has only been carried out on the model carbon, Spherocarb. The philosophy, however, behind these detailed surface studies on model carbons has always been to identify the correct kinetic *framework*, which can then be extended to other chars in the form of a parameterized engineering model.

The goal of this section therefore is to explore the ability of the Haynes model framework to describe typical data on a range of carbons from the oxidation kinetic database. There is only limited experimental guidance on how best to parameterize the model. Important model parameters most likely to vary from one carbon to the next are the mean and standard deviation of E_{des} and the parameters a and b in Eq. 9 that govern adsorption kinetics. The experiments of Lear[14] show similar temperature programmed desorption spectra for Spherocarb and Loy Yang coal char, with somewhat larger differences in transient chemisorption kinetics. We therefore attempt here to describe the disordered carbon data of Suuberg[4] and Madsen[5] by starting with the Spherocarb parameters and making small adjustments to the adsorption and, if necessary, desorption energy distributions to match the overall rate and pressure dependence.

Figure 5.7a compares Haynes model predictions to the Fig. 5.2a data of Suuberg et al.[4] taken over a factor of 200 in partial pressure. The final parameter set is identical to that for Spherocarb except the parameter "a" in Eq. 9 was reduced from 165 kJ/mol to 152 kJ/mol and the desorption distribution breadth, Δ_{des} , decreased from 60 kJ/mol to 45

kJ/mol. Figure 5.7b shows the results of similar fits to the coal char data of Madsen et al.[5]. These chars have global kinetic parameters that are similar to those for Spherocarb, though the absolute rates differ greatly. In this case adjustments were made only to parameter "a" (Eq. 9) yielding 153 kJ/mol (Spherocarb), 142 kJ/mol (Pitt. coal), and 118 kJ/mol (lignite). All other parameters remain identical to those determined experimentally for Spherocarb. The model successfully predicts slight decreases in global order and activation energy as reactivity increases in the series Spherocarb < Pitt. #8 < Lignite char. The fit is not perfect, but the comparison is very encouraging, since only one parameter was adjusted ("a" in Eq. 9) to fit in essence three data features: the

Figure 5.7 Example application of the Haynes model framework to the oxidation kinetics of polymer and coal chars. **A.** The persistent power-law behavior observed by Suuberg et al.[4] on a polymer char is well described by the Haynes model with $a = 139$ kJ/mol in Eq. 9 and $\Delta_{des} = 45$ kJ/mol. **B.** Extension to coal char data of Madsen[5], (see also Hecker et al.[6]) by variation in "a" from 153 to 118 kJ/mol. All other parameters are identical to those determined experimentally for Spherocarb[11].

absolute rate, n_{global} , and the pressure dependence of n_{global} . The Haynes model with only small perturbations to the experimental Spherocharb parameters is clearly capable of describing typical low temperature char oxidation data at and above atmospheric pressure.

Another useful modeling target is the graphite data of Tyler et al.[1], who published a particularly thorough study of the reaction order over a wide pressure range (see Fig. 5.8). The reported reaction orders vary *gradually* with oxygen pressure in a manner that is intermediate between the power-law and Langmuir limiting cases. Lear[14] found that the TPD distribution on Graphon, a highly annealed carbon black, has a similar mean E_{des} to disordered carbon, but is significantly narrower ($\Delta E_{des} = 35$ kJ/mol vs. 60 kJ/mol for Spherocharb and 65 kJ/mol for Loy Yang coal char[14]). Lear also showed that oxygen chemisorption on Graphon is about 10% of that on Spherocharb, per unit mass of carbon. Therefore we attempted here to fit the Tyler global kinetic data starting with the Spherocharb parameters and varying the distribution width, ΔE_{des} , and the number of active sites per unit mass.

Figure 5.8 shows the result. The Haynes model can predict the Tyler et al. reaction orders and their gradual shift with pressure. The same parameters give a good prediction of the global activation energy, (258 kJ/mol vs. 268 kJ/mol measured), and an exact match (by design) to the absolute rate. Here two parameters (ΔE_{des} and $N_{Graphon}/N_{Spherocharb}$) were adjusted to fit four data features: n , the pressure dependence of n , E , and the absolute rate, R . The final parameters were $\Delta E_{des} = 17$ kJ/mol and 0.033 mol-active-sites/kg. The active site number is a factor of 30 below the disordered carbon Spherocharb, which is not unreasonable, while the distribution breadth is significantly smaller than for the disordered chars, as expected. The narrower distribution is responsible for the weak pressure dependence of order (the distribution is not broad enough for full n^{th} -order kinetics) and the generally low orders, which arise from contraction of the low- E_{des} tail, giving a smaller value of $A_{<0.5}$ in Eq. 18 and thus fewer adsorption-limited sites). This fit offers an attractive explanation for the generally lower orders for graphitic carbons relative to disordered carbons in Fig. 5.1 — it is a natural consequence of reduced heterogeneity in these low-defect-density materials.

Chapter 5 Conclusions

A sufficient explanation for the long-standing paradox of persistent, high fractional order in the carbon/oxygen reaction is surface heterogeneity. Simple models of surface heterogeneity, whether intrinsic or induced, predict power-law behavior over wide ranges of partial pressure if the breadth of the activation energy distribution for adsorption and/or desorption is large. The available measurements of desorption activation energy distributions show more than enough breadth for this power-law behavior to be generally expected for non-graphitic carbons, in accordance with experimental observations.

The heterogeneous surface model of Haynes is a promising framework for describing the major features in the low-temperature carbon oxidation database. The Haynes model with minor perturbations to the original parameters determined experimentally for Spherocharb is capable of describing the rates, reaction orders, and pressure dependence of reaction order for several literature datasets on polymer and coal chars, along with the known existence of stable oxide. The Haynes model is also capable of predicting the lower orders and the gradual change in reaction order with pressure for graphitized carbon black, a behavior that is intermediate between power-law and Langmuirian kinetics. The model predicts these features as the direct consequence of the narrower distribution of site energies for the more homogeneous highly annealed carbon forms.

It is impractical to carry out the detailed surface characterization to fully define heterogeneous surface models for each carbon material of technological interest. Such models do provide, however, much needed theoretical underpinning for the commonly used power-law kinetic form, and the Haynes formulation in particular offers a new framework for the development of robust parameterized engineering models for practical application. More work is needed on the oxide oxidation step, $O_2 + C(O) \rightarrow products$ before a comprehensive model is available for application to the literature database. This reaction step is likely to be significant at the lowest temperatures of interest, where its kinetics will be superimposed on the power law behavior described here. The oxide

oxidation step is likely complex, but is nominally first order in O_2 , and its influence may thus provide an explanation for the significant number of unity and near unity orders seen in the literature compilation of Fig. 5.1.

Figure 5.8. Graphite oxidation data of Tyler et al.[1] showing reaction order that varies gradually with pressure (closed diamonds), a behavior that is transitional between the single-site Langmuir form (dashed grey curve) and power-law kinetics. The solid curve gives the predictions from the Haynes model with $\Delta_{des} = 18$ kJ/mol, and an active site number ratio ($N_{Graphon} / N_{Spherocarb}$ of 1/30). All other parameters were the same as determined experimentally for Spherocarb [11].

Chapter 5 References

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CHAPTER 6

CHAR COMBUSTION REACTIVITIES FOR A SUITE OF DIVERSE SOLID FUELS

Introduction and Background

Concern over the potential effects of global warming is driving a diversification in solid fuel selection — a shift from almost sole reliance on coal to a broader fuel mix encompassing organic matter of quite diverse origin and composition. To support this effort, comparative studies are needed in which large sets of these diverse alternate fuels are burned under standard conditions chosen to reveal intrinsic fuel-to-fuel differences in each of the fundamental combustion subprocesses: pyrolysis, char oxidation, mineral transformations, and pollutant formation.

For coals, the char combustion subprocess has been extensively studied and reviewed [1-4], and the major reactivity trends have been established through comparative studies employing a range of coals, including studies below 1000K[5-8] and at flame temperatures [9,10]. There are no comparable studies on large sets of alternate fuels, although the recent literature does contain valuable information on individual fuels [11-14] or small sets of fuels of interest in a particular region [15-18]. It is not known if any of the compositional trends and correlations derived from coal studies have relevance to biomass and other alternate fuel types.

The goal of the present work was to measure char combustion reactivities for a large set of traditional and alternative solid fuels under standardized low-temperature conditions, free from the influence of mass- and heat-transfer processes (Zone I). A secondary goal was to identify possible quantitative relationships between char reactivity and parent fuel properties. To gain a deeper understanding of the origin of char reactivity in this data set, the sample suite was augmented by a series of char-forming chemical reagents and model materials that are nearly free of the inorganic contamination that is ubiquitous in practical solid fuels.

Materials and Experimental Procedures

A suite of 31 materials was assembled for this study (see Table 6.1), including 20 solid fuels and 11 organic model materials chosen for their low levels of potentially catalytic inorganic matter. Each of the 31 raw materials was pyrolyzed in a benchtop tube furnace at 700°C for 1 hour using a thin bed of sample spread in an oblong alumina boat, purged with flowing high-purity helium (600 cc/min). Seventeen of the raw materials were also pyrolyzed at 1000°C for 1 hour to investigate the effect of heat treatment temperature. The subsequent chars were crushed and sieved to obtain a 75-106 μm size fraction for study. Because of the enormous reactivity range within this sample suite (over four orders of magnitude), it is not practical to measure all reactivities at a common temperature. Non-isothermal thermogravimetric analysis (TGA) was therefore carried out using a Cahn TG-2141 apparatus fed with dry air (21% oxygen) at 40 cc/min and atmospheric pressure. Char samples of 3-10 mg were spread as a thin bed on a platinum pan to avoid mass- and heat-transfer effects. Time, sample temperature, and mass were continuously recorded as the sample temperature was raised first to 105°C to drive off any moisture, then at 7 K/min to 950°C, at which point complete burnout was achieved for all samples. All reactivity measurements were made in triplicate and the mean values reported.

A subset of 14 of the 700°C chars was chosen for surface area measurements. Some fresh (unreacted) chars exhibit strong molecular sieving behavior in which the nitrogen and carbon dioxide surface areas are grossly different, an effect that is typically eliminated by only slight oxidative conversion [19,20]. For such chars, the proper assignment of area is ambiguous and the nitrogen area of the fresh char may be not at all representative of its values during most of the burnout process. To avoid this problem, chars slated for vapor adsorption measurements were first partially reacted by slow air oxidation in a tube furnace to conversions from 15-35% — close to the 20% at which the reactivity indices were derived (see below). Each of these chars was outgassed for 20 hours at 300°C, followed by measurement of 80-point vapor adsorption isotherms in nitrogen at 77K and in carbon dioxide at 195K, from which surface areas were computed using the BET theory.

Definitions of Standard Reactivity Indices

The non-isothermal TGA profiles were used to extract standard char reactivities reported here in two different but essentially equivalent forms:

1. Critical temperature values, T_{cr} , defined as the temperature at which the combustion rate first equals 0.05 g/min-g-initial-char. Other researchers have reported T_{cr} values [7] defined in a similar manner[†] as a convenient reactivity index that does not require kinetic assumptions.
2. Reactivity values, R , as burning rates in air at a standard reference temperature (T_{ref}) of 500°C, defined as:

$$R \equiv \left(\frac{1}{m} \frac{dm}{dt} \right) e^{\left(\frac{E}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right)} \quad [1]$$

where m , dm/dt , and T are determined at here 20% conversion, daf. The exponential term brings the raw rates to a common temperature for convenient fuel-to-fuel comparison.

This temperature normalization was made using an activation energy of 35 kcal/mol (146 kJ/mol), a typical value for Zone I char oxidation [2,8,21,22]. The use of a single activation energy is not a significant disadvantage of this particular reactivity index, because activation energies vary over only a modest range for the low- temperature, disordered chars of interest in this study, and because the standard reference temperature is chosen near the center of the range of actual temperatures, making the temperature correction term inherently small. Indeed there is an excellent correlation between T_{cr} and R as shown in Figure 6.1, so either index may serve as a valid expression of the relative reactivity of different chars in the sample suite.

Results

Standard reactivities as T_{cr} and/or R values are presented in Table 6.1 and Figs. 6.2 and 6.3. Reactivities of the 1000 °C chars are presented in Figure 6.3. Surface areas are presented in Table 6.1 and are cross-plotted against reactivity in Figure 6.4. The nitrogen and carbon dioxide surface areas of the chars at 20% conversion are generally similar, indicating the absence of strong molecular sieving effects, which would have complicated the interpretation.

Table 6.1 Sample Suite of Solid Fuels and Organic Model Substances: Properties^b and Char

Reactivities

Sample	ash	VM	C	H	O	N	S	Al	Ca	Fe	K	Mg	Na	Ni	Si	V	N ₂ Area ^c	CO ₂ Area ^c	T _{cr} ^j	log ₁₀ R ^f 700°C	log ₁₀ R ^f 1000°C
	dry %	dry %	daf %	daf %	daf %	daf %	daf %	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	m ² /g	m ² /g	K	sec ⁻¹	sec ⁻¹
Microcrystalline ^a Cellulose	0.05	90.71	41.86	6.42	51.68	0.02	0.02	<10	<5	<10	<40	<10	59	<1	12	<1	547.0	645.1	900	-4.35	-4.91
Synthetic RDF	19.84	71.32	41.95	6.46	51.55	0.02	0.02	23600	120	74	<40	44	253	1	62400	<1	335.5	353.3	905	-4.41	-4.84
Sucrose, C ₁₂ H ₂₂ O ₇ ^a	-	-	42.08	6.50	51.40	<0.01	<0.01	<100	<100	<100	<100	<100	<100	<100	<100	<50	592.1	638.0	900	-4.35	-4.58
Dried Sludge	0.06	76.36	42.37	6.54	48.01	3.05	0.03	67	983	289	480	218	452	<1	256	<1	-	-	838	-3.48	-
Corn Stalk	3.24	74.77	43.99	6.28	48.93	0.70	0.09	106	1900	130	15300	1600	41	<1	2380	<1	213.5	327.1	701	-1.70	-2.67
Wheat Straw	9.43	68.76	44.23	6.39	48.63	0.60	0.15	70	1720	52	15500	1140	72	<1	7880	<1	258.4	320.5	716	-2.12	-3.34
Rice Hulls	16.16	63.64	44.59	6.36	48.70	0.29	0.05	52	650	170	7880	400	72	7	71800	<1	-	-	751	-2.69	-
Hardwood	0.57	80.19	45.80	6.20	47.82	0.15	0.03	166	1470	270	1450	380	71	<1	954	<1	-	-	781	-3.07	-3.18
Bagasse Sachurum	3.82	78.43	45.92	6.26	47.60	0.17	0.05	3100	648	3700	1300	440	206	15	8770	8	-	-	873	-3.98	-
Pinus Radiata	0.22	79.44	46.05	6.31	47.58	0.04	0.02	170	408	240	738	150	77	<1	910	<1	-	-	845	-3.80	-
Softwood	0.46	76.14	46.14	6.32	46.01	1.48	0.05	220	700	250	997	217	1590	<1	745	<1	-	-	781	-3.08	-
Populus Deltoides	0.63	80.46	46.43	6.11	47.32	0.08	0.06	<10	2450	295	2360	300	68	<1	644	<1	434.3	458.0	762	-2.82	-
C ₂₂ H ₃₈ O ₇ ^{a,g}	-	-	63.73	9.16	26.85	<0.01	0.25	<100	<100	<100	<100	<100	<100	<100	<100	<50	386.8	504.2	912	-4.51	-5.05
Beulah (ligA) ^d	-	-	73.14	4.46	20.59	1.00	0.82	6000	18000	6100	500	5600	6600	0	5000	14	161.1	320.2	730	-2.44	-3.83
Polycarbon. Resin ^a	-	-	75.48	5.69	18.81	<0.01	0.01	<100	<100	<100	<100	<100	<100	<100	<100	<50	-	-	848	-3.85	-
Phenol-for. Resin ^a	-	-	77.76	5.96	16.22	0.05	<0.01	<100	<100	<100	<100	<100	<100	<100	<100	<50	-	-	886	-4.20	-4.81
Illinois #6 (hvCb) ^d	-	-	78.11	5.44	9.73	1.32	5.39	16000	5900	23000	2500	800	800	14	37000	3	-	-	823	-3.59	-4.46
Rosebud (subB) ^d	-	-	78.19	4.22	15.21	1.05	1.33	13000	13000	8500	500	2600	1200	<1	23000	2	-	-	765	-2.90	-
Koonfontain (mvb)	12.65	26.47	78.72	4.78	13.79	1.99	0.71	22600	6330	2630	689	1940	278	8	25400	16	-	-	904	-4.08	-
C ₃₀ H ₁₈ O ₄ ^{a,h}	-	-	79.69	4.19	16.05	0.01	0.06	<100	<100	300	<100	<100	100	<100	500	<50	-	-	847	-3.80	-
Fluid Coke	0.05	6.17	87.38	2.41	5.14	2.57	2.50	37	102	307	<10	20	136	476	193	477	-	-	951	-4.66	-5.07
Tire Bits	-	-	87.63	7.57	2.55	0.39	1.87	2200	2700	1500	500	600	400	200	5000	<50	-	-	931	-4.53	-4.89
Delayed Coke	0.05	11.04	87.80	3.96	1.41	1.43	5.40	17	47	213	<10	11	52	198	67	501	-	-	911	-4.39	-
Pocahontas (lvb) ^d	-	-	89.87	4.90	3.31	1.14	0.78	6000	600	7000	400	800	500	7	7000	9	113.5	136.2	974	-4.94	-
Lykens Valley (an) ^d	-	-	90.33	4.01	4.30	0.80	0.56	18000	400	3300	4600	600	200	17	29000	21	324.8	384.8	961	-4.88	-
Lei Yang (an)	22.35	5.64	90.47	2.01	5.86	0.72	0.93	27800	6250	6900	5790	1440	2730	19	46700	41	169.8	197.2	975	-5.01	-5.15
Petroleum Pitch ^a	-	-	94.50	5.09	0.19	0.00	0.22	-	-	-	-	-	-	-	-	-	-	-	974	-4.97	-
AR-HP Pitch ^{a,e}	-	-	95.13	4.87	0.00	0.00	0.00	-	-	-	-	-	-	-	-	-	141.1	175.1	966	-4.90	-5.76
AR-MP Pitch ^{a,e}	-	-	95.13	4.87	0.00	0.00	0.00	-	-	-	-	-	-	-	-	-	132.5	161.6	964	-4.90	-5.97
Graphite Powder ^a	-	-	96.30	0.38	<0.10	0.87	2.45	100	100	500	<100	<100	<100	100	200	280	-	-	1052	-5.54	-5.55
Graphite Rods ^{a,i}	-	-	100.0	0.00	0.00	0.00	0.00	1	2	1	0	0	1	0	7	0	5.05	6.15	1201	-6.39	-6.15

^a model materials selected for low amounts of potentially catalytic impurities

^b elemental analyses performed by Huffman Laboratories (Golden, CO) unless otherwise noted

^c multi-point BET surface areas of chars (He, 1 hr, 700°C) at 20% conversion (daf)

^d elemental analysis reported by Department of Energy Coal Bank at Penn State data sheets

^e synthetic mesophase pitches from naphthalene polymerization, high (HP) and medium (MP) grades; elemental analysis reported by manufacturer, Mitsubishi Gas Chemical

^f standard reactivity at 500°C in air of chars prepared at 700°C or 1000°C, as labeled

^g L-ascorbic acid 6-palmitate

^h 2,2'-dimethyl-1,1'-bianthraquinone

ⁱ elemental composition reported by vendor (Aldrich)

^j critical temperatures for the chars prepared at 700 °C

Trends in reactivity with fuel type are most easily identified using Figure 6.2, where we see that reactivities of the 700°C chars vary by almost 5 orders of magnitude under identical conditions. Considering only the practical solid fuels, the reactivities still span over 3 orders of magnitude, from high-rank coal chars (lowest reactivity) to corn stalk chars (highest reactivity). The 1000°C chars in Figure 6.3 show a similar data pattern, but with just over 3 orders of magnitude total variation in reactivity. A strong correlation is seen between reactivity and carbon (daf) content of the vitrinite-rich coals, as been observed previously [5,6,10]. This trend has no relevance for the biomass fuels, however, which cluster closely in composition (40%-50% daf carbon), while their reactivities span almost 3 orders of magnitude. Carbon content is a very poor indicator of biomass reactivity. By analyzing the data in Table 1 it can be further stated that no organic composition variable (C,H,O,N,S) provides enough information for making even a crude estimate of biomass char reactivity.

Figure 6.1. Correlation between the two reactivity indices reported in this work: critical temperatures, T_{cr} , and standard reactivities at 500 °C in air, R . For interconversion between the two indices one can use the following empirical expression: $\log_{10}R = -12.6 - 2.77 \cdot 10^{-2}T_{cr} + 9.97 \cdot 10^{-6}T_{cr}^2$

[†] Charpenay et al.[7] use a combustion rate of 0.065 min⁻¹ to define T_{cr} , but some samples in the present study never achieved rates this high at the chosen heating rate and gas environment

It is quite notable in Figure 6.2 that the model materials, chosen for their lack of inorganic impurities, all have reactivities that lie in a relatively narrow band in the low reactivity region. These non-catalytic char reactivities show almost no composition dependence between 40% and 80% carbon (daf), but do fall away above 90% carbon (daf). Overall, the patterns revealed in Figure 6.2 strongly suggest that organic composition is secondary to other factors determining reactivity in the char of precursors below 80% carbon (the majority of practical solid fuels). The next section examines reactivity/property relations in more detail.

Reactivity / Property Relations

The goal of this section is to investigate quantitative relationships between reactivity and properties of the parent material, focusing on the larger data set of 700°C chars. Statistical software (SPSS Inc.) used for multivariate linear regression revealed positive correlations with statistical significance between reactivity and three properties: wt-% K, Ca, and Mg. In addition a negative correlation was found between reactivity and wt-% carbon (daf). A simple linear correlation based on these four variables, however, does not provide an adequate description of the data set. Such blind statistical analyses are easy to perform, but make no use of insights gained from decades of research on combustion and fuel chemistry. Therefore, we pursued a hybrid approach that combines statistical analysis with chemical insights derived from literature data on different fuel classes. We begin by expressing the reactivity as a sum of two independent contributions:

$$R = R_{carb} + R_{cat} \quad [2]$$

where R_{carb} represents reaction on non-catalytic (carbon) active sites[23] and R_{cat} represents reaction on catalytic active sites [22], assumed to be independent, parallel processes. The existence of the narrow model substance band on Figure 6.2 suggests that variations in R_{carb} are only a small part of the total reactivity variation for fuels up to up to 80% carbon (daf) content. We therefore, as an approximation, define a single, non-catalytic baseline reactivity shown in Figure 6.2 that establishes the model parameter R_{carb} as a function of the parent material carbon content. This same line implicitly

Figure 6.2 Master plot of measured reactivities for chars prepared at 700 °C from the 31 precursors plotted as the percentage carbon content of the parent material (daf). The thick dashed line shows a strong correlation between reactivity and rank among vitrinite-rich coals, as reported in other oxidation kinetic studies[5,6,10]. The dotted lines define a relatively narrow region that encompasses all of the model materials that are nearly free of potentially catalytic inorganic matter. The lower dotted line is taken as a non-catalytic baseline in the model discussed in the section on reactivity / property relations.

defines R_{cat} as the difference between the measured reactivity and R_{carb} , the non-catalytic baseline value.

The primary challenge is to investigate relations between the catalytic residual, R_{cat} , and fuel properties. Studies involving demineralization and/or direct catalyst addition clearly reveal which elements are intrinsically catalytic for char oxidation: Group I metals, Group II metals, and many transition metals including V, Ni, and Fe, which have a particular importance in some solid fuels [5,22,24-27]. A spliced empirical relation for the non-catalytic baseline is:

$$\log_{10}R_{carb} = -4.1 - 6.25 \cdot 10^{-3}(\text{wt-\% C}), \text{ for wt-\% C} \leq 80$$

$$\log_{10}R_{carb} = -4.52 - 2.11 \cdot 10^{-7} \exp[0.16(\text{wt-\% C})], \text{ for wt-\% C} > 80$$

Figure 6.3 Master plot of measured reactivities for chars prepared at 1000 °C from a 17-sample subset of the 31-sample suite. The absolute reactivities are generally lower, but the fuel-to-fuel differences fall in a pattern very similar to the 700 °C chars in Figure 6.2. Literature data from Jenkins et al.[5] on coal chars prepared under similar conditions is shown for comparison.

Figure 6.4 Cross plot of reactivity vs. total char surface area (N_2 BET) for pure and noncatalytic materials (left hand side) and for all samples (right hand side). Circles (pure materials) are the nearly-inorganic-free model substances from Table 1; Triangles (non-catalytic materials) are samples containing significant amounts of inorganic matter, but predicted by dispersion arguments to react in a primarily non-catalytic mode (see section on reactivity/ property relations).

Another key consideration is catalyst dispersion, or particle size, which is expected to vary greatly across the spectrum of solid fuels. Although dispersion is continuum variable, one can consider two important limiting cases: (1) *granular dispersion*—particulate matter of supramicron dimension arising from extraneous matter or bulk additives in the fuels, and (2) *nanophase dispersion* — finely dispersed particulate matter of submicron dimensions in chars originating from nanophase or atomically dispersed metals in the parent materials that have partially sintered during carbonization [22]. This highly active material may originate as dissolved salts in plant water, as cations exchanged on carboxylic sites, or as organometallic compounds with essential function (e.g. chlorophyll, porphyrins). Granular material has low catalytic activity by virtue of its low surface area [28], which suggests the relation:

$$R_{cat} = \varnothing(K_{nano}) + \varnothing(Ca_{nano} + Mg_{nano}) + \varnothing(V_{nano}) \quad [3]$$

Here M_{nano} indicates the wt-fraction (ppmw) of the nano-dispersed or atomically dispersed form of catalytic metal, M , present in the parent fuel, and α_K , α_{Ca} , and α_{Mg} are specific activity coefficients to be determined from statistical analysis of the data. Although Na, Ni, and Fe are known catalysts for char oxidation[26,29], they are not observed to make statistically significant contributions to reactivity in this particular sample set and thus cannot be included in Eq. [3]. The alkaline earth metals are grouped together because our statistical analysis revealed a strong cross-correlation, making any attempt to distinguish the separate effects of Ca and Mg statistically meaningless. Studies employing metal addition have reported similar specific activities for Ca and Mg [26], so their linear combination here with equal weight is a useful approximation.

Before α_K , α_{Ca} , and α_{Mg} can be determined, specific rules are needed for estimating the degree of catalyst dispersion in the various fuel classes. In coals, mineral matter is a combination of granular material and atomically dispersed material [30,31], with the major source of atomically dispersed matter in the form of cations exchanged on carboxylic sites [22,31]. The compilation of literature data in Figure 6.5 shows the carboxylic site density is strongly dependent on coal rank. For the hybrid chemical/statistical model we use the correlation shown in that figure to estimate carboxylic site density from wt-% carbon (daf) and carry out a stoichiometric calculation to determine what fraction of the K, Ca, and Mg in the sample is needed to saturate those -COOH sites. This simple two-step correlative technique gives a reasonable estimate of K_{nano} , Ca_{nano} , and Mg_{nano} for use in Eq. [3].

Dispersion of metals in biomass is also a mixture of granular and atomically dispersed forms [32-35]. In most plants, however, potassium salts are essential nutrients, and a high fraction of the potassium (80-90%) is either water soluble or ion-exchangeable [32,33,35,36]. Most calcium also tends to be water soluble or ion-exchangeable, indicative of high dispersion. An exception is sugar cane bagasse, which is washed during processing and has lost soluble salts [33,35]. For purposes of the model we take the group I and II metals in biomass to be finely dispersed with the exception of bagasse in which the remaining matter is taken to be primarily granular. For the non-biomass

alternate fuels, we take the inorganic components in tire fuel to be granular, while the vanadium in cokes is taken to be nano-dispersed, since it originates as atomically dispersed material within porphyrin structures in petroleum [37].

The preceding set of dispersion rules, along with Eqns. [2] and [3], the baseline function in Figure 6.2, and the carboxylic correlation in Figure 6.5, define the hybrid chemical/statistical model. Application of the model to our data set leads to the final correlation and the optimal least-squares values of β_1 , β_2 , and β_3 shown in Figure 6.6. The now complete hybrid model provides a link between parent fuel elemental composition and char reactivity at 500°C in air for chars prepared at 700°C from arbitrary and diverse organic precursors.

It is clear from this analysis that catalysis plays a dominant role in the low-temperature reactivity of chars prepared at 700°C. Through examination of the data patterns in Figure 6.3, this same conclusion appears to hold for the chars prepared at 1000°C. Using the final values of β_1 , β_2 , and β_3 as sensitivity coefficients, it can be stated that as little as 44 ppmw of nano-dispersed potassium or 270 ppmw of nano-dispersed Ca or Mg is sufficient for the catalytic component of reactivity to exceed the non-catalytic component for materials below 80 wt-%-carbon (daf). With these sensitivities it is difficult to rule out catalytic effects in all but the most pure materials. Indeed, the ICP sensitivity limits for some of the nearly pure model materials are 100 ppmw, so residual catalysis may even be important for some of these compounds, such as $C_{30}H_{18}O_4$ and polycarbonate resin, which lie in the upper region of the model substance band in Figure 6.2. Among the practical solid fuels, only the very highest rank coals (with no -COOH sites) are adequately approximated as non-catalytic. Previous studies employing acid demineralization have also suggested that catalytic effects are significant for most coals[5], although questions have often been raised about collateral effects of strong acids on the organic matrix. The present work reaches the same conclusion by statistical inference from reactivity data without the need for aggressive mineral solvents.

Figure 6.5 Compilation of literature data on the abundance of carboxylic groups in coals of various rank. Sources: circles are data from Ihnatowicz in [38], diamonds are data from Morgan and Jenkins [31], squares are data from Blom in [38], and triangles are data from Otake and Walker [39]. The fitted curve for use in the hybrid chemical/statistical model is: $(\text{wt-\% O as -COOH}) = 3.051 \cdot 10^{-9} \exp[-0.2706 \text{ wt-\% C (daf)}]$ for $\text{wt-\% C} < 90$. Above 90 wt-% C, -COOH site density is taken to be 0 in the model.

Figure 6.6 Comparison of measured reactivities with reactivities given by the hybrid chemical/statistical model. The plot contains every solid fuel and model material listed in Table 1 except graphites (which cannot be meaningfully described as 700 °C chars) and the Permian southern hemisphere coal (for which Figure 6.6 does not contain relevant data on carboxylic sites). The model reactivity is equal to:

$$R = R_{carb} + \square(K_{nano}) + \square(Ca_{nano} + Mg_{nano}) + \square(V_{nano})$$

where R_{carb} is the baseline function in Figure 6.2, $\square = 7.9 \cdot 10^{-7}$, $\square = 1.3 \cdot 10^{-7}$, and $\square = 3.1 \cdot 10^{-8}$, where the nano or atomically dispersed metals are measured in ppmw of the parent fuel.

Chapter 6 Conclusions

1. Char combustion reactivities at 500 °C in air from a diverse set of fuels and organic model compounds vary over 4 orders of magnitude when chars are prepared at 700 °C and over 3 orders of magnitude when chars are prepared at 1000 °C. Reactivities correlate poorly with organic elemental composition and poorly with char surface area.
2. Specially-acquired model materials with minute amounts of inorganic matter exhibit low reactivities that fall in a narrow band as a function of wt-% carbon. Reactivities in this sample subset correlate reasonably well with total char surface area.
3. A hybrid chemical/statistical model explains most of the observed reactivity variation based on four variables: the amounts of nano-dispersed K, nano-dispersed (Ca+Mg), elemental carbon (wt-% daf), and nano-dispersed vanadium, listed in decreasing order of importance. Catalytic effects play a very significant role in the oxidation of most practical solid fuel chars. Some degree of reactivity estimation is possible using only elemental analyses of parent fuels, but only if correlative techniques make use of the existing body of knowledge on the origin, form and dispersion of inorganic matter in various fuel classes.

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CHAPTER 7

GASIFICATION KINETICS IN PRESSURIZED CO₂

Background

As indicated previously, several technologies, such as Integrated Gasification Combined Cycle (IGCC), Pressurized Fluidized Bed Combustion (PFBC) and Pulverized Coal Injection (PCI), have been identified as the most viable alternatives for the clean utilization of coal due to the use of combined cycles (Smoot and Smith, 1985; Smoot, 1998). These technologies operate at elevated pressure (e.g., 10-15 atm for PFBC, 15-25 atm for IGCC, and less than 5 atm for PCI). High pressure operation results in increased coal throughput, reduction in pollutant emissions, and enhancement of reactivity (Takematsu and Maude, 1991; Harris and Patterson, 1995). Here we focus specifically on the kinetics of CO₂ gasification at elevated pressures.

The carbon-CO₂ reaction has been extensively investigated due to its importance in the overall carbon gasification scheme. The gasification process first involves the chemisorption of oxygen on the carbonaceous surface, followed by subsequent desorption as carbon oxides. There have been a number of experimental studies on the mechanism of CO₂ gasification (Mentser and Ergun, 1973; Blackwood and Ingeme, 1960; Walker, 1986; Reif, 1952). Perhaps the most widely accepted mechanism in the literature for the carbon-CO₂ reaction at low pressures was proposed by Ergun and Mentser (1973). It is believed that CO₂ adsorption on the surface of the char, followed by CO desorption are the principal steps, *i.e.*

where C(O) is a carbon-oxygen surface complex, and C_f is a vacant carbon active site. Under pseudo-steady-state conditions, in an atmosphere of CO₂, reaction [R.1] is driven to the right, populating an active site and producing one CO molecule. The second step is the desorption of the carbon-oxygen surface complex to yield another molecule of CO, thereby, generating a new active site, and completing the overall stoichiometry:

The carbon-CO₂ gasification reaction is affected by a number of factors. Among them, CO₂ partial pressure plays an important role in determining the rate. It is widely accepted

that the pressure dependence on the gasification rate at low pressure can be adequately expressed by the well-known *Langmuir-Hinshelwood* type expression, whether the reaction is catalyzed (Kapteijn and Moulijn, 1983) or not (Mentser and Ergun, 1973), *i.e.*,

$$r = \frac{k_1 C_t P_{CO_2}}{1 + \frac{k_1}{k_2} P_{CO_2} + \frac{k_1}{k_2} P_{CO}} \quad (1)$$

where C_t is the total number of active sites, and P_{CO} and P_{CO_2} are the partial pressures of CO and CO_2 , respectively.

The effect of CO_2 pressure on the gasification rate has been investigated by a number of workers (Dutta *et al.*, 1977; Harris and Smith, 1989; Ye *et al.*, 1998; Nozaki *et al.*, 1992; Zhang and Calo, 1996). However, the overall apparent reaction order for the carbon- CO_2 reaction still remains a matter of controversy. Most workers report that the gasification rate is first order with respect to CO_2 pressure below atmospheric pressure, and zeroth order at elevated pressures. Turkdogan and Vinters (1969) reported CO_2 gasification rates in the absence of CO in the reactor feed gas to be half-order at pressures less than 10 atm, and zeroth order at pressures of 10-20 atm. Koenig *et al.* (1985,1986) also reported half-order behavior. The latter workers proposed a model involving dual-site adsorption and dissociation of CO_2 to explain this behavior. The two-site adsorption of CO_2 can be expressed as:

where C^* is a two-site surface complex. One possibility for the structure of C^* is a lactone-type surface species.

On the other hand, the gasification data of Johnson (1979) for a bituminous coal char in CO/CO_2 mixtures over the range of 2-35 atm, showed a decreasing effect of CO_2 partial

pressure on the gasification rate at high pressures. A similar trend was reported by Golovina (1980), who reported first order behavior at near-atmospheric pressure, trending to zeroth order over the 3-10 atm range, followed by decreasing gasification rate with CO₂ partial pressure in the 20-40 atm pressure range.

However, some other notable exceptions have also been reported. Blackwood and Ingeme (1960) measured the gasification rate at elevated pressures, and proposed the following mechanism based on their data:

This mechanism results in a rate expression (Blackwood and Ingeme, 1960):

$$r = \frac{kP_{\text{CO}}^2}{1 + aP_{\text{CO}} + bP_{\text{CO}_2}} \quad (2)$$

which indicates a second order dependence on CO₂ partial pressure over a certain range.

Another factor to be considered is the inhibition by CO evident in Eqns. (1) and (2). It is known that product CO can have a retarding effect on the rate of reaction (Turkdogan and Vinters, 1970; Shufen and Ruizheng, 1994; DeGroot and Shafizadeh, 1984; Blackwood and McTaggart, 1959). Two theories have been advanced to explain this effect of CO (Blackwood and Ingeme, 1960). Gadsby *et al.* (1948) suggested that CO can be adsorbed on the carbon surface and thus compete for active sites. The process is represented by the reaction:

Blackwood and Ingeme (1960) and Liu *et al.* (2000) included this step in their mechanisms to explain gasification rates at high pressures. The second possibility, which is the most supported in the literature (Mentser and Ergun, 1973; Reif, 1952; Harris and Smith, 1989; Ye *et al.*, 1998; Kapteijn *et al.*, 1991), is the oxygen-exchange mechanism:

which suggests that CO inhibition occurs not by adsorption, but rather *via* the reverse reaction between CO and chemisorbed oxygen.

Due to the questions still remaining, the effects of elevated CO₂ pressures on gasification reactivity and the inhibition effect of CO were investigated in a high pressure TGA.

Experimental

High pressure thermogravimetry

Gasification rate data were obtained using a high pressure, high temperature thermogravimetric apparatus manufactured by DMT (Deutsche Montan Technologie) capable of operating under pressures up to 40 bar and temperatures up to 1100°C. The TGA system consists of: (1) the entire TGA-reactor; (2) the gas supply for three reaction gases and the flushing or purge gas; (3) the expansion unit including the condenser; (4) separate bypasses for the permanent reaction gases; and (5) a computerized data acquisition and process control system that allows for the recording of temperature, pressure, gas flow rates, and sample mass. The software also allows for automated pressurizing and depressurizing, control of total and partial pressures, flow rates, and internal and external temperatures.

With this system, the gas mixture can be pre-adjusted without exposing the sample to a reactive environment, while the sample is maintained under a separate inert flowing atmosphere. This guarantees a minimum of weight signal disturbance during switching from one atmosphere to the other. A process flow diagram is presented in Figure 7.1, and an image of the DMT-TGA apparatus in Figure 7.2.

A cylindrical sample holder containing approximately 100 mg of sample was placed in the pressurized sample chamber. The system was pressurized with CO₂/N₂ or CO₂/CO mixtures. The reaction zone was heated to the desired temperature and the sample was then lowered into the reaction zone. Gasification measurements were made at the following conditions:

Total pressure: 1-20 atm

Total flow rate: 0.90 l/min

Char samples

A few different chars were investigated in this work. The Brown University samples were prepared from synthesized phenol-formaldehyde resin (all from the same batch), and Wyodak subbituminous coal samples obtained from the Penn State coal sample bank (DECS-26/PSOC-1566) (DECS, 1995). The fresh resin and coal were sieved to +35/-20 mesh (420 – 840 μm), and then pyrolyzed in a quartz tube furnace in flowing ultrahigh pure helium at 1273K for 2 h. The resultant particle size range of the resultant char was 250-360 μm . The resultant chars were then activated in oxygen at 793K; the resin char to approximately 6%, and the Wyodak char to about 10% burn-off.

Preparation of the Brigham Young University (BYU) samples is described elsewhere in this report. The ultimate analysis of these coals and char samples produced in the HPFFB and the atmospheric flat flame burner at BYU are given in Table 7A.1 in Appendix A. The resultant pore size distributions and surface areas are presented in Table 7A.2. The latter were obtained from the CO_2 adsorption/desorption isotherms (195K – dry ice in acetone bath) presented in Figures 7A.1-4, that were obtained at Brown University.

Results and Discussion

The effect of total CO_2 pressure

The effect of total pressure on the gasification rate was investigated at temperatures between 825 and 1100°C in the pressure range 1-20 atm in pure CO_2 for the phenolic resin char (PRC) and Wyodak coal char (WY). Arrhenius plots of the resin char and Wyodak coal char reactivities in CO_2 are presented in Figures 7.3 and 7.4, respectively. The results in Figure 7.3 show that the apparent activation energy *decreases* with increasing pressure. In addition, increasing pressure *increases* the reactivity, especially at low temperatures, but this effect *decreases* with increasing temperature, such that by 1373K, the effect of pressure is much less marked. These data are in disagreement with some classical models developed at atmospheric pressure and below that suggest

asymptotic behavior of reactivity with increasing CO₂ pressure (Turkdogan and Vinters, 1969; Liu *et al.*, 2000; Frederick *et al.*, 1993).

In Figure 7.4 for the Wyodak coal char, it can be seen that the reactivity is almost unaffected by increasing total pressure up to about 15 atm. Above this pressure (20 atm) the reactivity *increases* considerably at temperatures < 900°C, and the apparent activation energy *decreases* with increasing total pressure ($P > 10$ atm). This behavior is most probably due to the presence of catalytic mineral matter impurities in the Wyodak coal char; e.g., calcium, which is known to catalyze the CO₂ gasification reaction. For example, Walker *et al.* (1979,1984) demonstrated that the reactivity of lignite chars is controlled primarily by the catalytic effect of calcium associated with carboxyl groups.

Some literature values for apparent activation energy and reaction order for CO₂ gasification for a variety of char types under various conditions are presented in Table 7.1. A summary of apparent activation energies for the resin char and Wyodak coal char obtained in the current work are presented in Table 7.2. These values agree reasonably well with some of the values reported in Table 7.1.

The effect of CO₂ partial pressure

The CO₂ partial pressure was varied from 100% to 40% at a total pressure of 15 atm by dilution with nitrogen. The gasification temperatures were 900°C for Wyodak coal char and 1000°C for the resin char.

In Figures 7.5 and 7.6 are presented plots of $\ln(r)$ vs $\ln(P_{CO_2})$ for resin char and Wyodak coal char, respectively, where r is the specific reactivity, defined as the mass loss rate, dm/dt , divided by the sample mass, m , at the time t :

$$r = \frac{1}{m} \left(\frac{dm}{dt} \right) = kP_{CO_2}^n \quad (3)$$

where k is the rate constant, P_{CO_2} is the CO₂ partial pressure, and n is the apparent reaction order.

As shown in both figures, the partial pressure has a significant effect on reactivity for both chars at the selected gasification conditions, with the reactivity *increasing* with increasing CO₂ partial pressure. From Eq. (3), the slope of the plot of $\ln(r)$ vs $\ln(P_{CO_2})$ is equal to the apparent reaction order, n . As shown in Figure 7.5 and 7.6, the apparent reaction order, n , is 0.45 ± 0.09 for the resin char and 0.68 ± 0.39 for the Wyodak coal char. It has been reported that the reaction order for CO₂ gasification is first order with respect to CO₂ partial pressure below atmospheric pressure (Gadsby *et al.*, 1948; Biederman *et al.*, 1976), and half order at higher pressures (Nozaki *et al.*, 1992; Turkdogan and Vinters, 1969). The reaction orders observed in the current work agree reasonably well with some of the values reported in Table 7.1.

A comparison of the reactivities for both chars as a function of CO₂ partial pressure is presented in Figure 7.7. Since the Wyodak coal char contains mineral matter impurities, its reactivity is significantly greater than that of the resin char, even at lower CO₂ partial pressures.

The inhibition effect of CO

It is known that CO can have an inhibiting effect on the CO₂ gasification rate (Turkdogan and Vinters, 1970; Shufen and Ruizheng, 1994; DeGroot and Shafizadeh, 1984; Blackwood and McTaggart, 1959). However, studies on the effect of CO on the CO₂ gasification rate reaction at elevated pressure are relatively limited (Blackwood and Ingeme, 1960; Frederick *et al.*, 1993). Gasification rate measurements were carried out in the pressurized microbalance at 900°C for the Wyodak coal char and 1000°C for the resin char. CO₂ and CO partial pressures were varied while holding the total pressure constant at 15 atm.

In Figures 7.8 and 7.9 are presented plots of $\ln(r)$ vs $\ln(P_{CO_2})$ for the resin char and Wyodak coal char, respectively, along with the data from Figures 7.5 and 7.6 for comparison. As shown, in Figure 7.8, for the same corresponding CO₂ partial pressures, the reactivity *decreases* considerably with increasing CO partial pressure, and the apparent reaction order *increases* significantly from 0.45 ± 0.09 in the absence of CO to

1.15 ± 0.23 in the presence of additional CO. These data demonstrate the strong inhibition effect of CO on the gasification reaction. Frederick *et al.* (1993) investigated the effect of CO on the CO₂ gasification reaction at 700°C and elevated pressures and reported an apparent reaction order of 0.88.

Similar trends were observed for the Wyodak coal char in Figure 7.9. As shown, the reactivity *decreases* considerably with increasing CO partial pressure for the same corresponding CO₂ partial pressures, and the apparent reaction order *increases* from 0.68 ± 0.39 in the absence of CO to 1.96 ± 0.44 in the presence of additional CO. This is suggestive of the behavior of the rate expression proposed by Blackwood and Ingeme (1960) which described results obtained at elevated pressures in the presence of 10% of CO:

$$r = \frac{kP_{CO_2}^2}{1 + aP_{CO} + bP_{CO_2}} \quad (4)$$

indicating a *second order* dependence on CO₂ partial pressure over a certain pressure range. In order to test this rate form further, plots of P_{CO_2}/r vs $1/P_{CO_2}$ at constant total pressure ($P_{CO_2} + P_{CO} = c = 15$ atm), varying the relative partial pressures of CO₂ and CO, should be linear if the data conform to Eq. (4); i.e.,

$$\frac{P_{CO_2}}{r} = \frac{1}{kP_{CO_2}} [1 + ac] + \frac{(b - a)}{k} \quad (5)$$

Plots of Eq. (5) for the Wyodak coal char and the PRC are presented in Figure 7.10. As shown, the Wyodak data do indeed appear to follow a relatively linear relationship, thereby indicating agreement with the kinetic rate form of Eqns. (4) and (5) originally proposed by Blackwood and Ingeme (1960). However, as is also as shown in Figure 7.10, the PRC data, do not appear to follow this same rate form at all. Instead, they appear to follow the more traditional first order Langmuir-Hinshelwood rate form of Eq. (2), which when plotted in a similar fashion as Eq. (5) becomes:

$$\frac{1}{r} = \frac{1}{kP_{CO_2}} [1 + ac] + \frac{(b - a)}{k} \quad (6)$$

Plots of Eq. (6) for both sets of data are presented in Figure 7.11. As shown, it is clear that the PRC data fit the form of Eqns. (2) and (6), while the Wyodak data do not.

The primary difference between these two chars is that the Wyodak coal char reactivity is controlled by mineral matter whereas the PRC is not. Most probably the oxygen transport capacity of mineral matter sites in the Wyodak coal char to active carbon sites results in apparent second order behavior, whereas the first order behavior of the PRC is more in concert with the traditional oxygen exchange mechanism discussed previously.

Comparisons of the reactivities of both chars as a function of CO_2 partial pressure are presented in Figure 7.12. As shown, the Wyodak coal char exhibits *greater* reactivity than the resin char for CO_2 partial pressures greater than 11.25 atm (75% CO_2) primarily due to the presence of catalytic mineral matter impurities. However, with an increase in CO partial pressure (> 3.75 atm, or 25% CO) the reactivity of the Wyodak coal char becomes less than that of the phenolic resin char. This is most probably related to the effects of CO chemisorption on mineral matter impurities as well, that serves to retard the surface oxygen transport process catalyzed by the mineral matter to active carbon sites. Consequently, not only do mineral matter impurities often control the reactivity of coal chars, but can also alter the mechanism and the resultant apparent rate form as well. Due to the elliptic nature of Langmuir-Hinshelwood rate expressions (Eqns. (2) and (4)) plus the almost certain energetic heterogeneity of char surfaces (e.g., see Calo and Perkins, 1987), the apparent reaction order for CO_2 gasification can vary over the range of zero to two. This is one of the reasons for the wide range of apparent reaction orders reported in the literature. Consequently, the development of robust rate expressions for a particular char still depends on obtaining reliable reaction rate data at conditions similar to what the char will experience in practice. This is one of the important themes of the current project.

BYU coal chars

Reactivity measurements were obtained for four coal chars (Knife River, Wyodak, Koonfontain, and Pittsburgh #8) produced at 1300K at atmospheric pressure (actually 0.85 atm in Utah) in an atmospheric flat flame burner facility at Brigham Young University (Zhang and Fletcher, 2001). The char samples were collected immediately above the luminous devolatilization zone of the flame. The size of coal particles ranged from 45 to 130 μm . Typical particles used in pulverized coal furnace applications had a mean diameter of $\sim 50 \mu\text{m}$. Particle heating rates were $\sim 10^5 \text{ K/s}$.

The resultant measured reactivities are presented in Figures 7.13-7.17 for these coal chars, and the apparent activation energies are summarized in Table 7.3. The results for the BYU Wyodak coal char presented in Figure 7.13 show that reactivity increases with CO_2 pressure, as expected. A summary plot of the reactivity data for both the BYU and BU Wyodak chars is presented in Figure 7.14. It is noted that these coal chars differ primarily in the heating rates at which they were prepared, and the “heat soak” time at the ultimate temperature. The BU samples in Figure 7.3 were produced in a tube furnace at very low heating rates at 1273K, whereas the samples in Figure 7.13 were prepared at about 1300K at heating rates on the order of 10^5 K/s . As shown, the BYU samples are much more reactive at higher temperatures, but their apparent activation energies are also greater, such that their reactivities become more comparable to the BU Wyodak samples at lower temperatures. Thus, the noted differences in reactivity are undoubtedly due to the considerably longer annealing times experienced by the BU chars (i.e., 2h in the tube furnace vs 50 – 100 ms in the flat flame burner), which significantly decreased the concentrations of active sites in the BU chars.

Similar reactivity behavior is noted for the Knife River lignite, the Koonfontain, and the Pittsburgh #8 coal chars in Figures 7.15, 7.16, and 7.17, respectively. For the Pittsburgh #8 char there was a very large increase in reactivity upon increasing the CO_2 pressure from 5 atm to 10 atm.

Chapter 7 Conclusions

CO₂ gasification reactivities were determined for a phenolic resin char and Wyodak coal char and the effects of total CO₂ pressure, CO₂ partial pressure, and the inhibition effect of CO on the reaction rate were investigated at elevated pressures. For both chars, the apparent activation energy *decreases* with *increasing* pressure. In the case of the resin char, higher pressure *increases* reactivity at low temperature, but this effect *decreases* with increasing temperature, such that by 1373K, the effect of pressure has *decreased* substantially. These data are in disagreement with some classical models developed at atmospheric pressure and below that suggest asymptotic behavior of reactivity with increasing pressure. For the Wyodak coal char, the reactivity is only modestly affected by increasing the total pressure up to 15 atm. This is attributed to the presence of mineral matter impurities in the Wyodak coal char; i.e., calcium, which is known to catalytically dominate the CO₂ gasification reaction.

These char samples were gasified in varying mixtures of CO₂ and nitrogen at a total pressure of 15 atm. The results show that char reactivity increases monotonically with CO₂ partial pressure for both chars. Since the Wyodak coal char contains mineral matter impurities, its reactivity is significantly higher than that of the resin char, even at lower CO₂ partial pressures.

The inhibition effect of CO on gasification rate was investigated for the phenolic resin char and Wyodak coal char in varying mixtures of CO₂ and CO at a total pressure of 15 atm. The reactivity *decreases* considerably with increasing CO partial pressure, and the apparent reaction order *increases* significantly from 0.45 to 1.15 for resin char and from 0.68 to 1.98 for Wyodak coal char. Kinetic analysis of these data show that the Wyodak coal char obeys a Langmuir-Hinshelwood-type rate form with both CO and CO₂ inhibition terms in the denominator and a numerator that is quadratic in CO₂ partial pressure (e.g., as proposed by Blackwood and Ingeme, 1960). The PRC data, on the other hand, are fit by a similar expression, but with a numerator that is first order in CO₂ partial pressure (e.g., as proposed by Mentser and Ergun, 1973). These differences in kinetic behavior are attributed to the surface oxygen transport capacity of the mineral matter in

the Wyodak coal char, most probably calcium (23.5 % of the ash by weight, on average; DECS, 1995).

The BYU coal char samples produced at high heating rates exhibited similar behavior; i.e., increasing reactivity with CO₂ partial pressure. The Wyodak coal char results indicate that the BYU chars were much more reactive at high temperatures than the BU samples, but exhibited larger apparent activation energies, such that their reactivities became more comparable to that of the BU Wyodak samples at lower temperatures. This was attributed to the high heating rate ($\sim 10^5$ K/s) and very short pyrolysis times (~ 100 ms) experienced by the samples in the BYU FFB. This did not allow any time for thermal annealing, and thus produced high concentrations of active carbon sites. Due to the elliptic nature of Langmuir-Hinshelwood rate expressions (Eqns. (2) and (4)) plus the almost certain energetic heterogeneity of char surfaces (e.g., see Calo and Perkins, 1987), the apparent reaction order for CO₂ gasification can vary over the range of zero to two. This is one of the reasons for the wide range of apparent reaction orders reported in the literature. Moreover, the char preparation conditions can have a very large impact on the resultant reactivities as well. Consequently, the development of robust rate expressions for a particular coal char still depends on obtaining reliable reaction rate data under preparation conditions and subsequent reaction conditions similar to what the char will experience in practice. This was one of the fundamental themes of this project.

Chapter 7 References

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**Table 7.1 Apparent activation energies and reaction orders for the
char-CO₂ gasification reaction.**

Sample	Temperature Range (K)	CO ₂ Partial Pressure (bar)	Apparent Activation Energy (kJ/mol)	Apparent Reaction Order	Reference
Coal char	1093-1158	1	251	–	Jiang and Radovic, 1989
Coke, char	923-1173	1	185-245	0.68	Harris and Smith, 1989
Coal char	993-1293	2	122	–	Shufen and Yuanlin, 1995
Lignite char	1073-1323	1	146-128	–	Sinag <i>et al.</i> , 2003
Olive residue char	1073-1223	0.2-0.5	133	0.43	Ollero <i>et al.</i> 2003
Australian coal char	987-1165	1	91	–	Ye <i>et al.</i> , 1998
Coal chars	1123	0.2-0.5 0.5-15 above 15	–	0.7 0.5 0.7	Nozaki <i>et al.</i> , 1992
Lignite char	1073-1223	10	149	0.34	Shufen and Riuzheng, 1994
Resin and coal chars	1073-1205	1	209-251	0.7 0.6	Zhang and Calo, 1996
Graphite	1050-1300	1	230-251	0.7	Overholser and Blakely, 1965
Graphite and coconut char	975-1475	10 ⁻³ -10	284.5	0.5	Turkdogan and Vinters, 1969

Table 7.2 Apparent activation energies for CO₂ gasification of the Brown University samples: resin char (PRC) and Wyodak coal char (WY) as a function of pressure.

Char Sample	Total Pressure (atm)	Apparent Activation Energy (kJ/mol)
PRC	1	178 ± 18
PRC	5	163 ± 16
PRC	10	149 ± 15
PRC	15	110 ± 11
PRC	20	107 ± 11
WY	1	161 ± 16
WY	5	164 ± 16
WY	10	155 ± 16
WY	15	138 ± 14
WY	20	94 ± 9

Table 7.3 Apparent activation energies for CO₂ gasification of the Brigham Young University samples as a function of pressure.

Char Sample	Total CO ₂ Pressure (atm)	Apparent Activation Energy (kJ/mol)
Wyodak	1	233 ± 23
Wyodak	5	198 ± 20
Wyodak	10	230 ± 23
Knife River	1	206 ± 21
Knife River	10	299 ± 30
Koonfontaine	1	336 ± 34
Koonfontaine	10	288 ± 29
Pittsburgh #8	1	198 ± 20
Pittsburgh #8	5	160 ± 16
Pittsburgh #8	10	468 ± 47

Figure 7.2 High pressure, high temperature thermogravimetric apparatus (DMT-TGA).

Figure 7.3. Arrhenius plots for phenolic resin char (PRC) as a function of total CO₂ pressure.

Figure 7.4. Arrhenius plots for Wyodak coal char (WY) as a function of total CO₂ pressure.

Figure 7.5. Specific reactivity of phenolic resin char (PRC) in CO₂/N₂ mixtures at 1000°C as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.6. Specific reactivity of Wyodak coal char (WY) in CO₂/N₂ mixtures at 900°C as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.7 Comparison of specific reactivities of phenolic resin char (PRC) and Wyodak coal char (WY) in CO₂/N₂ mixtures as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.8 Specific reactivity of phenolic resin char (PRC) in CO₂/CO mixtures at 1000°C as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.9 Specific reactivity of Wyodak coal char (WY) in CO₂/CO mixtures at 900°C as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.10 Test of quadratic kinetic model of Wyodak coal char and phenolic resin chars at a total pressure of 15 atm in CO_2/CO mixtures.

Figure 7.11 Test of first order kinetic model of Wyodak coal char and phenolic resin chars at a total pressure of 15 atm in CO_2/CO mixtures.

Figure 7.12 Comparison of specific reactivities of phenolic resin char (PRC) and Wyodak coal char (WY) in CO₂/CO mixtures as a function of CO₂ partial pressure at a total pressure of 15 atm.

Figure 7.13 Arrhenius plots for Wyodak (BYU) coal char as a function of total CO_2 pressure.

Figure 7.14 Arrhenius plots for Wyodak coal char as a function of total CO_2 pressure. The open symbols are for the Brown char, and the closed symbols for the BYU char.

Figure 7.15 Arrhenius plots for Knife River coal char as a function of total CO₂ pressure.

Figure 7.16 Arrhenius plots for Koonfontain coal char as a function of total CO₂ pressure.

Figure 7.17 Arrhenius plots for Pittsburgh#8 coal char as a function of total CO_2 pressure.

Appendix 7A.

Brigham Young University Coal Chars Characterized at Brown University

Table 7A.1. Ultimate analysis of BYU samples.

Coal/Char	Ultimate Analysis (wt%, daf)				
	C	H	N	S	O
Knife River Lignite Coal	51.697	3.516	0.789	1.062	42.937
1 atm Knife River Lignite Char	60.043	1.002	0.621	0.815	37.520
6 atm Knife River Lignite Char	58.427	1.836	0.705	0.993	38.040
10 atm Knife River Lignite Char	40.897	0.904	0.347	1.905	55.947
Wyodak SubB Coal	62.227	4.804	0.855	0.417	31.698
1 atm Wyodak Char	77.137	1.347	0.627	0.123	20.767
6 atm Wyodak Char	98.907	0.894	0.120	0.083	-0.003
10 atm Wyodak Char	75.600	1.135	0.359	0.136	22.770
Koonfontain Coal	71.035	3.970	1.992	0.373	22.631
1 atm Koonfontain Char	77.070	0.769	1.670	0.043	20.448
6 atm Koonfontain Char	79.975	1.753	1.893	0.315	16.065
10 atm Koonfontain Char	84.713	1.519	1.460	0.140	12.168
Pittsburgh #8 Coal	78.067	5.055	1.854	0.454	14.570
1 atm Pittsburgh #8 Coal Char	78.173	1.226	1.781	0.576	18.244
6 atm Pittsburgh #8 Coal Char	72.750	1.457	1.661	0.591	23.541
10 atm Pittsburgh #8 Coal Char	59.507	2.239	0.578	0.833	36.843

Table 7A.2. Porosity characterization from CO₂ adsorption isotherms.

Coal Char/Flat Flame Burner Pressure	Dubinin-Radushkevich Analysis			BET Analysis
	Mean Pore Width (nm)	Micropore Volume (cm ³ /g)	Micropore Surface Area (m ² /g)	BET Surface Area (m ² /g)
Knife River Lignite Char				
1 atm	1.51	0.167	387	317
6 atm	1.69	0.109	252	215
10 atm	4.05	0.092	192	162
Wyodak SubB Coal Char				
1 atm	1.59	0.215	499	426
6 atm	1.67	0.190	440	403
10 atm	1.76	0.035	81.7	93.2
Koonfontain Coal Char				
1 atm	1.91	0.160	373	197
6 atm	1.66	0.123	286	221
10 atm	1.64	0.162	376	314
Pittsburgh #8 Coal Char				
1 atm	1.60	0.163	378	213
6 atm	1.67	0.190	440	403
10 atm	1.68	0.117	271	237

Figure 7A.1. CO₂ adsorption/desorption isotherms (195K – dry ice in acetone bath) of Knife River lignite char prepared at different pressures at BYU.

Figure 7A.2 CO₂ adsorption/desorption isotherms (195K – dry ice in acetone bath) of Wyodak coal char prepared at different pressures at BYU.

Figure 7A.3 CO₂ adsorption/desorption isotherms (195K – dry ice in acetone bath) of Koonfontain coal char prepared at different pressures at BYU.

Figure 7A.4 CO₂ adsorption/desorption isotherms (195K – dry ice in acetone bath) of Pittsburgh #8 coal char prepared at different pressures at BYU.

CHAPTER 8

IMPLEMENTATION OF ADVANCED COAL COMBUSTION SUBMODELS INTO B&W'S CFD CODE

1 INTRODUCTION

The advanced coal combustion models, Chemical Percolation and Devolatilization (CPD) [Fletcher, 1992] and Carbon Burnout Kinetic (CBK) [Hurt, 1988] were modified as part of this project for inclusion in comprehensive computational CFD codes. These models were implemented as subroutines in B&W's proprietary CFD code, COMOSM. In order to realize the increased accuracy from these advanced models the coal/char constituent model was reformulated to allow variable rates of progress for different gaseous products during devolatilization and char oxidation. This report gives a technical specification for the interface between these models and related chemical processes and physical properties.

For consistency with the current software language conventions used in COMOSM both subroutines were converted to ANSI C with the revised versions submitted back to the originating authors. The change from FORTRAN to C follows the objected-oriented programming paradigm currently used in most major software development projects. For successful coupling to a CFD code, which solves the particle transport using a stiff ODE solver, it is necessary for the calls to the rate routines for the submodels to be idempotent (multiple calls to the subroutine yields the same result). The identification of the variables which constituted the descriptive states of the particles was a significant undertaking in the early part of the project. Further work is planned at B&W to further reduce the number of state variables by removal of variables which can be derived from independent variables thus reducing the amount of information which is to be transferred when particles are computed in parallel implementations.

2. THEORY

Particle Constituent Model

The coal composition is represented as water, ash and the principal organic elements (carbon, hydrogen, nitrogen, oxygen and sulfur). Prior to the implementation of the CPD model, the composition of coal was modeled with the constituents C, H, N, O, S, H₂O and ASH. The implementation of the CPD model necessitated the reformulation of the coal constituent model to include a new constituent C* which is used to partition the fuel carbon (carbon is partitioned between C and C*). The species C* is used to model the coal heat of formation such that the complete conversion of the Dry, Ash-Free (DAF) coal constituents (C, C*, H, N, O, S) to gaseous products produces the specified coal higher heating value.

The mass of the C* specie is assumed to be completely consumed during the devolatilization process. Only carbon in the form of C is allowed to remain since the heat of combustion of the constituent C is in good agreement with the measured heat of combustion of residual char samples (primarily composed of carbon). In the Arrhenius formulation all the DAF carbon is initially assigned to the C* constituent. Since the final devolatilization yield is specified a priori the C* is then converted to C (reaction 1) proportionally to the rate of devolatilization through equation 1.1. From a thermophysical perspective, C and C* are identical in both formulations, except for the heat of formation.

$$r_{C, \text{char}} = X_{C^*, \text{DAFF}}^0 r_{\text{devol}} \quad 1.1$$

where

$$X_{C^*, \text{DAFF}}^0 = \text{initial DAF coal carbon mass fraction } (kg_{C^*} / kg_{\text{DAFF}})$$

$$r_{\text{devol}} = \text{rate of devolatilization } (kg_{\text{DAFF}} / s)$$

When the CPD model is used the initial amount of the specie C* is modeled as the amount of initial carbon present in the form of labile bridges. The mass of this specie is assumed to be completely consumed during the devolatilization process at the rate of labile bridge transformation via equation 1.2.

$$r_C = -\frac{dC^*}{dt} \equiv -\frac{d\xi}{dt} \quad 1.2$$

where

$$\frac{d\xi}{dt} = \text{rate of labile bridge transformation } (kg_{DAFF} s^{-1})$$

The heat of formation of C* for both devolatilization submodels is determined from equation 1.3:

$$\Delta H_{f,C^*} = \frac{\Delta H_{comb} - \sum_{j=1, cons \neq C^*}^{N_{org. cons.}} \Delta H_{f,j} X_{j,DAFF}^0}{X_{C^*,DAFF}^0} \quad 1.3$$

where

$$\Delta H_{comb} = \text{heat of combustion of DAF coal } (J kg_{DAFF}^{-1})$$

$$N_{org. cons.} = \text{number of organic fuel constituents}$$

$$X_{j,DAFF}^0 = \text{initial DAF organic fuel constituent mass fraction } (\%)$$

$$X_{C^*,DAFF}^0 = \text{initial DAF C* mass fraction } (\%)$$

Particle Energy Balance

The particle energy balance is modeled as the sum of convective heat transfer between the local gas environment, radiative heat transfer from incident radiant energy and particle absorption/emission and energy transfer occurring through chemical reactions.

The governing equation for the particle energy balance is written as follows:

$$\frac{d}{dt}(m_p h_p) = Q_{conv} + Q_{rad} + \sum_{k=1}^{N_R} r_k \sum_{j=1}^{N_{gs}} (\bar{c}_{jk} \hat{h}_j(T_g) - \bar{c}_{jk} \hat{h}_j(T_p)) \hat{M}_j \quad 1.4$$

where

$m_p =$	particle mass (kg)
$h_p =$	particle enthalpy (J kg ⁻¹)
$Q_{conv} =$	convective heat transfer to the particle (W)
$Q_{rad} =$	radiative heat transfer to the particle (W)
$N_R =$	number of chemical reactions
$r_i =$	rate of reaction i (kg s ⁻¹)
$N_{gs} =$	number of gas species
$\nu_{jk} =$	stoichiometric coefficients of reactant species j
$\hat{h}_j =$	molar enthalpies (J kmol ⁻¹)
$T_g =$	gas temperature (K)
$\nu'_{jk} =$	stoichiometric coefficients of product species j
$T_p =$	particle temperature (K)
$\hat{M}_j =$	relative molecular weight (kg kmol ⁻¹)

Differentiation of the LHS by parts:

$$\begin{aligned} \frac{d}{dt}(m_p h_p) &= \frac{d}{dt} \left(\sum_{j=1}^{N_{cons.}} m_j h_j(T_p) \right) = \sum_{j=1}^{N_{cons.}} m_j \frac{dh_j}{dt} + \sum_{j=1}^{N_{cons.}} h_j \frac{dm_j}{dt} \\ &= m_p \frac{dh_p}{dt} + \sum_{j=1}^{N_{cons.}} \hat{M}_j \sum_{k=1}^{N_R} r_k (\nu'_{jk} \hat{h}_j - \nu_{jk} \hat{h}_j) \end{aligned} \quad 1.5$$

where

$N_{cons.} =$ number of solid constituents

Combining Eq. 1.4 with Eq. 1.5 results in

$$m_p \frac{dh_p}{dt} = Q_{conv} + Q_{rad} + \underbrace{\sum_{k=1}^{N_R} r_k \left(\sum_{j=1}^{N_{gs}} (\nu'_{jk} \hat{h}_j(T_g) - \nu_{jk} \hat{h}_j(T_p)) \right) \hat{M}_j + \sum_{j=1}^{N_{cons.}} (\nu_{jk} \hat{h}_j(T_p) - \nu'_{jk} \hat{h}_j(T_p)) \hat{M}_j}_{\dot{H}_k} \quad 1.6$$

where

$N_{gs} =$ number of gas species

Over the time interval Δt of numerical integration (Equation 1.7) the particle specific

heat is modeled as a constant:

$$m_p \frac{dh_p}{dt} = m_p \frac{d}{dt} \left[h(T_o) + \int_{T_o}^{T_p} c_p dT \right] = m_p c_p \frac{dT_p}{dt} \quad 1.7$$

where

$$\begin{aligned} c_p &= \text{heat capacity of the particle } (J kg^{-1} K^{-1}) \\ \frac{dT_p}{dt} &= \text{rate of change in particle temperature } (K s^{-1}) \end{aligned}$$

For small time steps, the error introduced by the assumption of constant specific heat during the time-step is negligible. The latent heat of phase change (moisture evaporation and devolatilization) must be accounted for in the heat of formations of reactants and products. Except for the thermophysical properties of tar, the latent heat of devolatilization is neglected since the gaseous products are formed from pure elemental constituents. To explicitly account for the latent heat of vaporization the constituent model would have to be modified to include solid constituents with heat of formations which realize the change in enthalpy when the solid constituents are released as gaseous products.

Convective Heat Transfer Rate : The convective heat transfer rate Q_{conv} is defined as:

$$Q_{conv} = h A_p (T_g - T_p) \quad 1.8$$

where

$$\begin{aligned} h &= \text{convective heat transfer coefficient } (W m^{-2} K^{-1}) \\ A_p &= \text{particle surface area } (m^2) \end{aligned}$$

The heat transfer coefficient h is defined as:

$$h = \frac{\phi \cdot Nu \cdot k_g}{d_p} \quad 1.9$$

where :

$$\begin{aligned} \phi &= \text{mass transfer number } (\phi) \\ Nu &= \text{Nusselt number } (\phi) \\ k_g &= \text{gas thermal conductivity } (W m^{-1} K^{-1}) \end{aligned}$$

The ϕ term represents the effects of high mass transfer on the convective heat transfer coefficient [Spalding, 1955], and is defined by the following equation:

$$\phi = B / (e^B - 1) \quad 1.10$$

where the transfer number B for heat transfer is defined by:

$$B = \frac{c_{Pg}}{2\phi d_p k_g} \left[\frac{dm_p}{dt} \right] \quad 1.11$$

where: c_{Pg} = gas heat capacity ($J m^{-1} K^{-1}$).

The Nusselt number is given by :

$$Nu_{ht} = 2 + 0.6 Re_d^{1/2} Pr^{1/3} \quad 1.12$$

where

Re_d = Reynolds number based on the particle diameter and relative velocity of continuous phase ($\square$)

Pr = Prandtl number ($\square$)

Currently the Prandtl number is approximated as 0.7. The gas thermal conductivity k_g is calculated based on the local film temperature T_{film} , modeled as the arithmetic mean:

$$T_{film} = \frac{T_g + T_p}{2} \quad 1.13$$

Radiative Heat Transfer Rate : The radiative heat transfer rate Q_{rad} is defined as:

$$Q_{rad} = \sigma_p A_p (\sigma_{bb} \square \square \cdot T_p^4) \quad 1.14$$

where

σ = Stefan-Boltzman constant ($5.67 \cdot 10^{-8} W m^{-2} K^{-4}$)

σ_p = particle emissivity ($\square$)

σ_{bb} = radiative flux to particle ($W m^{-2}$)

General Model Formulation

Material balances for Lagrangian particles are simply written as

$$\frac{dm_i}{dt} = \hat{M}_i \sum_{k=1}^{N_R} r_k \sum_{j=1}^{N_{cons.}} (\sigma_{kj} \square \sigma_{kj}) n_{ij} \quad 1.15$$

where

n_{ij} = moles of constituent i per mole of solid species j

$\hat{M}_i$ = molecular weight of constituent i

with initial conditions $m_i = m_i^o$ at the start of the particle trajectory, $t=0$, and

$m_p = \sum_{L=1}^{N_{cons.}} m_L$ is the total particle mass where $L = \{C, H, N, O, S, H_2O, Ash, C^*\}$.

Auxiliary transport equations for initial coal mass (m_{coal}^o) and initial char mass (m_{char}^o) may be required to determine particle properties (diameter, number concentration, surface area, density, etc.) used to calculate heterogeneous reaction rates. They are never used directly for overall mass and material balances.

For Lagrangian particles, these quantities are known a priori or determined later along the particle trajectory.

Overview of Particle Lifetime

The particle life is modeled as a sequence of particle conversion modes which are particle heat-up, moisture evaporation, devolatilization, char combustion and inert ash transport. For low-rank coals there may be overlap between the devolatilization and char combustion modes. Currently, the possible overlap is not accounted for in the particle conversion modes during Lagrangian calculations; overlap is permitted during Eulerian particle calculations.

Particle Heatup

During the particle heat-up period (before evaporation of moisture) the particle temperature typically increases due to convective and radiative heat transfer. The only particle property which varies during this period is the particle heat capacity which is temperature dependent.

$$m_p c_p \frac{dT_p}{dt} = Q_{conv} + Q_{rad} \quad 1.16$$

Moisture Evaporation Rate

The rate of evaporation is given by:

$$r_{evap} = N_{H_2O} A_p M_{H_2O} \quad 1.17$$

where

$$N_{H_2O} = \text{molar flux of vapor } (kmol m^{-2} s^{-1})$$

The molar flux of vapor is given by:

$$N_{H_2O} = A_p \frac{Nu k_{gas}}{d_p \rho_{gas} c_{p, gas}} (C_{H_2O,s} - C_{H_2O,\infty}) \quad 1.18$$

where

$$C_{H_2O,s} = \text{water vapor concentration at the particle surface } (kmol m^{-3})$$

$$C_{H_2O,\infty} = \text{water vapor concentration in the bulk gas } (kmol m^{-3})$$

The water vapor concentration at the particle surface is modeled as :

$$C_{H_2O,s} = \frac{P_{sat}(T_p)}{R_{gas} T_p} \quad 1.19$$

Coal Devolatilization

The CPD model has been incorporated into COMOSM for the prediction of coal devolatilization. This model uses percolation theory and correlations based on readily available proximate and ultimate analyses to model the coal particle devolatilization. Modifications were made to the original CPD formulation by [Perry, 2000] to predict evolution of nitrogen species. Modifications were made during this project to allow the routine to be used to return rate of progress of gaseous species evolution at the beginning of an arbitrary time step. The heterogeneous reaction steps for the transformation of particle constituents are given by reactions 4-15:

Light gas reactions:

Tar reactions:

In the CPD model, the coal structure breaks down into a distribution of char, metaplast, tar and light gases. The metaplast fraction is released into the gas phase as tar or cross-linked into the char structure. The CPD model distributes the fraction of the particle mass released as light gases into H₂O, CO, CO₂, CH₄, and “other” through the use of a look-up table based on the work of Xu and Tomita [ref]. In Eq. 1.20 the “other” fraction has been modeled as C₂H₄.

$$f_{lg} = f_{H_2O} + f_{CO} + f_{CO_2} + f_{CH_4} + f_{C_2H_4} \quad 1.20$$

H₂S evolution is assumed to be proportional to light gas release according to Eq. 1.21. The fraction of particle mass evolved as HCN (f_{HCN}) is given directly as an output of the CPD model. The NH₃/HCN ratio is available as a user specified constant.

$$f_{H_2S} = f_S^o \cdot f_{lg} \cdot \frac{\hat{M}_{H_2S}}{\hat{M}_S} \quad 1.21$$

With the current constituent model in COMOSM it is necessary to specify the elemental composition of the tar which is fixed during the devolatilization of the particle. This is accomplished in a preprocessing step by integrating the light gas evolution over an arbitrary temperature profile and setting the tar composition equal to the original particle composition less the composition of the light gas products (char and tar are assumed to be equal in composition). The molecular weight of the tar is obtained from the preprocessing step as the average tar molecular weight calculated from the CPD model. Since the thermochemical information of species is specified into COMOSM using JANAF polynomial databases, the hydrocarbon portion of the tar is input as a newly created specie “TAR” and the residual oxygen and sulfur are represented as separate species. It is currently considered not worthwhile to create an agglomerate specie which contains all the organic elements since this can not be represented as a JANAF database and would require a major development effort.

The total particle mass for an arbitrary time step is determined by Eq. 1.22.

$$m_{p,t+\Delta t} = m_{p,t} + \Delta t \cdot \left[\frac{dm_{p,tar}}{dt} + \frac{dm_{p,lg}}{dt} + \frac{dm_{p,H_2S,HCN\&NH_3}}{dt} \right] \quad 1.22$$

The elemental composition is determined from Eq. 1.23 for each element e

where $e = \{C, H, N, O, S\}$

$$m_{pe,t+\Delta t} = m_{pe,t} + \Delta t \cdot \left[\frac{dm_{pe,tar}}{dt} + \frac{dm_{pe,lg}}{dt} + \frac{dm_{pe,H_2S,HCN\&NH_3}}{dt} \right] \quad 1.23$$

The amounts of elements C, H, O & S remaining after the complete light gas evolution are determined by Eqs. 1.24-1.27 where the f indicates the total final yield of each product and the r indicates the remaining fraction of the elemental composition which is either released as tar or incorporated into the final char solid matrix.

$$f_C^r = f_C^o \left[f_{CO} \cdot \frac{\hat{M}_C}{\hat{M}_{CO}} + f_{CO_2} \cdot \frac{\hat{M}_C}{\hat{M}_{CO_2}} + f_{CH_4} \cdot \frac{\hat{M}_C}{\hat{M}_{CH_4}} + f_{C_2H_4} \cdot \frac{2 \cdot \hat{M}_C}{\hat{M}_{C_2H_4}} + f_{HCN} \cdot \frac{\hat{M}_C}{\hat{M}_{HCN}} \right] \quad 1.24$$

$$f_H^r = f_H^o \left[f_{H_2O} \cdot \frac{\hat{M}_{H_2}}{\hat{M}_{H_2O}} + f_{CH_4} \frac{4 \cdot \hat{M}_H}{\hat{M}_{CH_4}} + f_{C_2H_4} \frac{4 \cdot \hat{M}_H}{\hat{M}_{C_2H_4}} + f_{HCN} \frac{\hat{M}_H}{\hat{M}_{HCN}} + f_{H_2S} \frac{2 \cdot \hat{M}_H}{\hat{M}_{H_2S}} \right] \quad 1.25$$

$$f_O^r = f_O^o \left[f_{CO} \cdot \frac{\hat{M}_O}{\hat{M}_{CO}} + f_{CO_2} \cdot \frac{\hat{M}_{O_2}}{\hat{M}_{CO_2}} + f_{H_2O} \cdot \frac{\hat{M}_O}{\hat{M}_{H_2O}} \right] \quad 1.26$$

$$f_S^r = f_S^o \left[f_{H_2S} \frac{\hat{M}_S}{\hat{M}_{H_2S}} \right] \quad 1.27$$

The particle elemental composition due to tar and "other" light gas evolution is given by Eqs. 1.28-1.35. As previously stated, the stoichiometric coefficients $\square_{tar}$ are given as input. The rates of particle elemental conversion in the following equations are the modifications which were made to the CPD model as part of this project and are tracked internal to the CPD model. The rate of nitrogen conversion uses existing expressions already present in the CPD model.

$$\frac{dm_{p_{C,tar}}}{dt} = \left[\frac{dm_{p_{tar}}}{dt} \right] \left[\frac{dm_{p_{N,tar}}}{dt} \right] \square_{C,tar} \quad 1.28$$

$$\frac{dm_{p_{C,lg}}}{dt} = \frac{dm_{p_{lg}}}{dt} \cdot \left[\frac{X_{CO} \cdot \hat{M}_C}{\hat{M}_{CO}} + \frac{X_{CO_2} \cdot \hat{M}_C}{\hat{M}_{CO_2}} + \frac{X_{CH_4} \cdot \hat{M}_C}{\hat{M}_{CH_4}} + \frac{X_{C_2H_4} \cdot 2 \cdot \hat{M}_C}{\hat{M}_{C_2H_4}} \right] \quad 1.29$$

$$\frac{dm_{p_{H,tar}}}{dt} = \left[\frac{dm_{p_{tar}}}{dt} \right] \left[\frac{dm_{p_{N,tar}}}{dt} \right] \square_{H,tar} \quad 1.30$$

$$\frac{dm_{p_{H,lg}}}{dt} = \frac{dm_{p_{lg}}}{dt} \cdot \left[\frac{X_{CH_4} \cdot 4 \cdot \hat{M}_H}{\hat{M}_{CH_4}} + \frac{X_{H_2O} \cdot 2 \cdot \hat{M}_H}{\hat{M}_{H_2O}} + \frac{X_{C_2H_4} \cdot 4 \cdot \hat{M}_H}{\hat{M}_{C_2H_4}} \right] \quad 1.31$$

$$\frac{dm_{p_{O,tar}}}{dt} = \left[\frac{dm_{p_{tar}}}{dt} \right] \left[\frac{dm_{p_{N,tar}}}{dt} \right] \square_{O,tar} \quad 1.32$$

$$\frac{dm_{p_{O,lg}}}{dt} = \frac{dm_{p_{lg}}}{dt} \cdot \left[\frac{X_{CO} \cdot \hat{M}_O}{\hat{M}_{CO}} + \frac{X_{CO_2} \cdot 2 \cdot \hat{M}_O}{\hat{M}_{CO_2}} + \frac{X_{H_2O} \cdot \hat{M}_O}{\hat{M}_{H_2O}} \right] \quad 1.33$$

$$\frac{dm_{pS,tar}}{dt} = \frac{dm_{p,tar}}{dt} - \frac{dm_{pN,tar}}{dt} \Delta_{S,tar} \quad 1.34$$

$$\frac{dm_{pS,lg}}{dt} = 0 \quad 1.35$$

The source terms for the gas phase conservation equations may be derived from rates of progress given in eqs. 1.36-1.43 with the particle conversion rates and fractional distribution determined by the CPD model.

$$r_{CH_4,lg} = \frac{dm_p}{dt} \cdot f_{CH_4} \quad 1.36$$

$$r_{C_2H_4,lg} = \frac{dm_p}{dt} \cdot f_{C_2H_4} \quad 1.37$$

$$r_{CO,lg} = \frac{dm_p}{dt} \cdot f_{CO} \quad 1.38$$

$$r_{CO_2,lg} = \frac{dm_p}{dt} \cdot f_{CO_2} \quad 1.39$$

$$r_{H_2O,lg} = \frac{dm_p}{dt} \cdot f_{H_2O} \quad 1.40$$

$$r_{HCN,lg} = \frac{dm_p}{dt} \cdot f_{HCN} \quad 1.41$$

$$r_{H_2S,lg} = \frac{dm_p}{dt} \cdot f_{H_2S} \quad 1.42$$

$$r_{tar} = \frac{dm_p}{dt} \cdot f_{tar} \quad 1.43$$

During devolatilization the particle diameter changes due to coal particle swelling. For sub-bituminous coals volatile evolution proceeds at a slow rate long after the initial yield due to internal cracking and distillation processes. The initial particle mass is given by:

$$m_p^o = m_{pH_2O}^o + m_{pash}^o + m_{pcoal,dry}^o \quad 1.44$$

Devolatilization Termination Criteria: Since the current implementation doesn't allow overlap of stages it is necessary to specify the criteria for the termination of the devolatilization. In particular, low-rank western coals continue to devolatilize, albeit at a slower rate for long periods after the labile bridges are consumed. The criteria adopted was to terminate the devolatilization stage if 1) all the labile bridges have been destroyed:

$$\mathbf{\xi} = 0 \quad 1.45$$

and if the rate of O₂ diffusion to the particle is greater than the rate of devolatilization:

$$r_{diff} = \frac{2 D_{ab} A_p M_{O_2} C_{H_2O}}{m_p d_p} \quad 1.46$$

where:

A_p = particle area (m^2)

m_p = particle mass (kg)

d_p = particle diameter (m)

D_{ab} = binary diffusivity of O₂ in N₂ ($m^2 s^{-1}$), given by:

$$D_{ab} = 2.851 \cdot 10^{-4} \left[\frac{T_p + T_g}{2} \right]^{1.65} P_{Atm} \quad 1.47$$

where:

P_{Atm} = ambient pressure (Atm)

Char Oxidation

The CBK model was implemented as a submodel in COMOSM in order to obtain more accurate predictions of char burnout. The CBK was developed specifically to account for the reduction in char reaction rates through thermal annealing and ash inhibition effects which cause char conversion to be overpredicted in the submodel based on the formulation of Field.

Since the bulk of the organic char matrix is carbon and relative changes in the stoichiometric coefficients are thought to have a negligible impact on predictions the

stoichiometric distribution of the products is held constant relative to the initial stoichiometric distribution at the onset of char oxidation. The char reaction mechanism is given by reactions 15-22:

Char carbon reacts to form CO and CO₂ with a molar ratio determined by:

$$\frac{N_{CO}}{N_{CO_2}} = A_C \cdot e^{\frac{E_c}{RT_p}} \quad 1.48$$

The rates of reactions 16 & 17 are determined directly from the rate of char combustion q_c obtained from the CBK model according to eqs. 1.49-1.50 as:

$$r_{CO, char} = \frac{N_{CO}}{N_{CO} + N_{CO_2}} \cdot q_c \cdot \frac{dp^2}{2} \quad 1.49$$

$$r_{CO_2, char} = \frac{N_{CO_2}}{N_{CO} + N_{CO_2}} \cdot q_c \cdot \frac{dp^2}{2} \quad 1.50$$

The rates of reactions 18-23 are obtained by maintaining the initial char stoichiometric distribution according to eqs. 1.51-1.55.

$$r_{H_2O, char} = \frac{1}{2} (r_{CO, char} + r_{CO_2, char}) \cdot \frac{m_{p,H}}{m_{p,C}} \quad 1.51$$

$$r_{O_2, char} = (r_{CO, char} + r_{CO_2, char}) \cdot \frac{m_{p,O}}{m_{p,C}} \quad 1.52$$

$$r_{SO_2, char} = (r_{CO, char} + r_{CO_2, char}) \cdot \frac{m_{p,S}}{m_{p,C}} \quad 1.53$$

$$r_{N_2, char} = (r_{CO, char} + r_{CO_2, char}) \cdot \frac{m_{p,N}}{m_{p,C}} \cdot (1 - f_{NO, char}) \quad 1.54$$

$$r_{NO, char} = (r_{CO, char} + r_{CO_2, char}) \cdot \frac{m_{p,N}}{m_{p,C}} \cdot f_{NO, char} \quad 1.55$$

The particle density during char combustion is determined through the char burning mode according to Eq. 1.56.

$$\frac{\rho}{\rho_{char}^o} = \frac{m_p}{m_{p, char}^o} \quad 1.56$$

The particle diameter is determined by Eq. 1.57.

1.57

$$\frac{d_p}{d_{p, char}^o} = \left(\frac{m_p}{m_{p, char}^o} \right)^{1/3} \quad 1.57$$

RESULTS

Sandia CDL

To test the accuracy of the devolatilization reactions of COMOSM using the CPD model the laminar flow experiments conducted in the Sandia CDL were modeled [Fletcher, 1992]. A 2D model was developed for the calculations consisting of a 3x1000 element mesh. The measured gas temperature and velocity profiles were approximated with polynomials which were subsequently used to initialize the elements of the model. The particle trajectory was then calculated while holding the gas temperature, velocity and composition constant. Shown below are the predictions for a single particle (115 μm) and measured temperatures (106-125 μm) of New Mexico Blue #1 in the nominal 1050 K gas temperature environment. In Figure 1 it is seen that the predicted particle temperatures are in reasonable agreement.

Figure 8.1. Predicted and Measured Particle Temperatures for New Mexico Blue #1 (PSOC-1445D) in 1050 K Gas Environment.

To understand the particle temperature the components of the particle energy transfer equation are computed for each time-step during the integration of the particle trajectory. It is observed in Figure 2 that initially the heat of reaction is endothermic which corresponds to the evaporation of moisture. During the late stages of devolatilization (around $z = 0.15$ m) the formation of the gaseous products from the solid fuel constituents causes the prediction of an exothermic reaction enthalpy. These exothermic transformations account for the predicted particle temperature overshoot shown in Figure 1.

Figure 8.2. Predicted Energy Transfer for New Mexico Blue #1 (PSOC-1445D) in 1050 K Gas Environment.

The predicted rates of progress for each of the devolatilization reactions is shown in Figure 3. Several reactions occur in parallel during the devolatilization. Future internal development at B&W will modify the constituent model to incorporate organic forms of oxygen (carbonyl, carboxyl and hydroxyl) and hydrogen (hydrogen and aliphatic) so that the transformation of the solid fuel reactants to gaseous products provides a better thermochemical model (less exothermic/endothermic) of the devolatilization process.

Figure 8.3. Predicted Rates of Progress for Devolatilization Constituents for New Mexico Blue #1 (PSOC-1445D) in 1050 K Gas Environment.

BYU PC Combustion Validation Cases

The introduction of the CPD and CBK models has brought the PC combustion modeling capabilities up to the state-of-the-art. During the design and implementation of the submodels, a decision was made to permit the new models to co-exist and to be applied interchangeably with the existing heterogeneous submodels for devolatilization and char oxidation – models of Ubhayaker, et al. (1975) and Field (1967), respectively. In addition

to providing a transition, this approach allows a side-by-side comparison of the models and their various permutations.

Table 1 – Description of Cases

Case	Devolatilization model	Char oxidation model
1 : ubhay-field	Ubhayaker	Field
2 : cpd-field	CPD	Field
3 : cpd-cbk	CPD	CBK

Initial comparison of the models were made using a 2-D, axisymmetric, non-swirling, PC combustion case described in several references (Fiveland et al., 1984, Fiveland and Jessee, 1994). Since the new submodels are only permitted with Lagrangian particles, the various permutations of the case only use this particle mode. Three model permutations are considered and are summarized in Table 1.

All cases were run with version 8.11.8 of COMOSM and all used the following models/methods:

- 1) k-epsilon turbulence model
- 2) SIMPLE algorithm for gas-phase flow solution
- 3) S4 discrete ordinate method for radiation heat transfer
- 4) Eddy dissipation gas-phase combustion model
- 5) Upwind advection scheme for all Eulerian transport equations

The operating conditions are detailed in the previously mentioned references. The 2-D axisymmetric domain was discretized using a non-uniform orthogonal mesh of 870 cells.

For the different cases, the results of axial velocity (U1), mixture temperature (TF), and oxygen (O₂), carbon dioxide (CO₂), and carbon monoxide (CO) concentrations are compared. For the three cases, the results are included in Figures 4-6, respectively.

In comparing the predictions, the biggest difference is the increased levels of CO₂ and higher temperatures for the cases using the CBK submodel. The Field model only reacts fuel carbon to CO while the CBK model reacts a portion of the fuel carbon to CO₂. This

results in higher temperature. The characteristics of the case, namely its 1-D nature and adiabatic boundaries, contribute significantly to the degree of variation in the predictions. Thus, these relatively large variations will not likely be seen in the analysis of commercial utility equipment. Nevertheless, the case is useful in highlighting the differences in the various heterogeneous reaction submodels.

Table 2 – Predicted Exit Values for BYU cases.

Case	Gas temp. (K)	CO (% kmol-i/kmol)	CO ₂ (% kmol-i/kmol)	O ₂ (% kmol-i/kmol)
1 : ubhay-field	2220	0.33	13.14	5.65
5 : ubhay-cbk	2294	0.10	14.16	4.34
6 : cpd-cbk				

Exit values for the cases are shown in Table 2. Included in the table are gas temperature, and CO, CO₂, and O₂ concentrations (mole fractions). The differences are largely attributed to the before-mentioned differences in the differences in char reaction products.

The CPU times for the three cases are displayed in Table 3. The activation of the CBK model in case 2 increases the CPU time by approximately 12%. The activation of the CPD model in case 3 increases the CPU time by approximately 353%. This may be expected since both the CPD and CBK models are more technically sophisticated than their respective counterparts. This increase in CPU time may be mitigated in the future by applying parallel processing and/or increasing the efficiency of the submodel calculations. The CPU times are all for 1000 global solution iterations. All cases were run on a Linux Cluster with 2.8 GHz Intel Xeon chips and Red Hat 8.0.

Table 3 – CPU Times for BYU cases.

Case	CPU time (s)*	increase over base
1 : ubhay-field	869	-
2 : ubhay-cbk	974	12%
3 : cpd-cbk	3936	353%

* the value represents the system time

The convergence history for the case 1 is shown in Figures 7. The momentum and mass residuals initially drop by three orders of magnitude over the first 300 iterations. Then, the stochastic nature of the particle dispersion takes over and the residuals level out. Lower levels may be achieved by increasing the sampling rate for the particle trajectories (i.e., number of trajectories) or relaxing the particle source terms. The residual histories for the other three cases exhibit similar characteristics and thus are not shown here.

Figure 8.4 - State Contours for Case 1 (Ubhay-field).

Figure 8.5 - State Contours for Case 2 (Ubhay -cbk).

Figure 8.4 - State Contours for Case 3 (cpd-cbk).

Figure 8.7 - Residual History for Case 1 (ubhay-field).

RECOMMENDATIONS

It is recommended that the coal constituent model in COMOSM be modified to incorporate functional groups for the functional groups containing oxygen (hydroxyl, carbonyl, carboxyl) and aliphatic H (Ar-CH₃)

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NOMENCLATURE FOR CHAPTER 8

A_p	=	particle surface area	(m^2)
c_p	=	heat capacity of the particle	$(J\ kg^{-1}\ K^{-1})$
C^*	=	Carbon in labile bridges	$(\%)$
$\frac{dT_p}{dt}$	=	rate of change in particle temperature	$(K\ s^{-1})$
ΔH_i	=	heat of reaction i	$(J\ kg^{-1})$
ϵ_p	=	particle emissivity	$(\%)$
f	=	fraction of particle mass	$(\%)$
h	=	convective heat transfer coefficient	$(W\ m^{-2}\ K^{-1})$
h_{fg}	=	latent heat of vaporization of water	$(J\ kg^{-1})$
k_g	=	gas thermal conductivity	$(W\ m^{-1}\ K^{-1})$
$\hat{M}_j$	=	relative molecular weight of constituent i	$(kmol\ kg^{-1})$
m_p	=	mass of the particle	(kg)
N_{gs}	=	number of gas species	
n_{ij}	=	moles of constituent i per mole of solid species j	
N_R	=	number of chemical reactions	
Nu	=	Nusselt number	$(\%)$
Q_{conv}	=	convective heat transfer to the particle	(W)
Q_{rad}	=	radiative heat transfer to the particle	(W)
Q_{rxn}	=	effect of phase change and chemical reactions on particle temperature	(W)
$\dot{r}_i$	=	rate of reaction i	$(kg\ s^{-1})$
σ	=	Stefan-Boltzman constant	$(5.67 \cdot 10^{-8}\ W\ m^{-2}\ K^{-4})$
ϕ	=	correction factor	$(\%)$
ϕ_{bb}	=	radiative flux to particle	$(W\ m^{-2})$
T_g	=	gas temperature	(K)
ν'_{jk}	=	stoichiometric coefficients of product species j	
ν_{jk}	=	stoichiometric coefficients of reactant species j	

CHAPTER 9

CONCLUSIONS

This multi-organization, multi-investigator project made significant progress in creating the necessary computer tools and fuel database entries for simulation of next-generation coal-based, fuel-flexible combustion and gasification processes. The main issue for pyrolysis is the effect of pressure for coals of various rank. By generating chars in both atmospheric and pressurized flat-flame burners (up to 15 atm), the team found a number of important trends. Volatiles yield decreases with increasing pressure, a trend that we also predicted using the CPD model using only the elemental composition and ASTM volatiles yields of the parent coals as changeable input parameters that relate to coal chemical structure. The H/C and O/C ratios in the resulting chars initially increase with increasing pressure, but remain relatively constant at pressures from 6 to 15 atm.

Swelling ratios of the lignite chars were less than 1.0, and only about 1.3-1.8 for the bituminous coals. All coal chars showed slight increases in swelling behavior as pressure increased. The swelling behavior observed for the Pitt #8 coal char at each pressure was lower than reported in high pressure drop tube experiments, supporting earlier work at atmospheric pressure showing that particle swelling decreases as heating rates approach 10^5 K/s. Both high pressure and low heating rate tend to increase swelling factors to values greater than those now used to describe atmospheric pc combustion.

Total char surface area, a parameter used in some char combustion models but not others, was found to decrease with increasing pressure. Char reactivities also decreased, when expressed on a per gram basis, but were found to be nearly constant on a per unit total surface area basis. We can thus expect high pressure chars to be somewhat less reactive, primarily due to loss of surface area, associated perhaps with decreased tar vaporization at pressure.

High-pressure, high-temperature char combustion experiments were also performed and the results analyzed with a combination of Fluent and the CPD and CBK submodels. The char oxidation rate was observed to increase with increasing total pressure. A different value of E or A_{30} was necessary for each pressure condition for each coal, meaning that a one-point calibration is necessary before CBK/E or CBK8 is capable of predicting char burnout at different pressures. The result obtained here that char reactivity increases with increasing total pressure is different than reported by some investigators. Some of that difference may be due to the fact that many previous investigators produced their starting char at atmospheric pressure only, rather than at the pressure where reactivity was measured (as was done in this study).

The work on pressurized combustion kinetics included a critical review and theoretical treatment of the global, power-law form and advanced, multi-step forms. One result is the first theoretical justification for the long-standing paradox of persistent, high fractional order in the char/oxygen reaction is surface heterogeneity. Simple models of surface heterogeneity, whether intrinsic or induced, predict power-law behavior over wide ranges of partial pressure if the breadth of the activation energy distribution for adsorption and/or desorption is large. The heterogeneous surface model of Haynes is a promising framework for describing the major features in the low-temperature carbon oxidation database including the persistent power-law behavior. More work is needed on the oxide oxidation step, $O_2 + C(O) \rightarrow products$ before a comprehensive model is available for application to the literature database.

The new theoretical work in this project sufficient underpinning to justify the use of the power-law form in practical char combustion modeling. The use of this form has practical advantages, but to date has lacked a fundamental basis and has led to much controversy and confusion in the field. There continues to be interest in the development and applications of more detailed rate expressions. If the field proceeds in that direction, the work carried out here suggests that the common 2-step Langmuir form is unsuitable, as it cannot predict the high fractional orders almost universally seen at low temperature. A possible promising direction is the use of three-step or four-step semi-global

mechanisms incorporating O₂-complex reaction as described here in Chapter 4. It remains to be seen if the added complexity relative to power-law approaches will allow this a popular approach in design applications.

This project also examined the *gasification* mechanisms at elevated pressure. CO₂ gasification reactivities were determined for a phenolic resin char and Wyodak coal char and the effects of total CO₂ pressure, CO₂ partial pressure, and the inhibition effect of CO on the reaction rate were investigated at elevated pressures. The results show that char reactivity increases monotonically with CO₂ partial pressure and the apparent activation energy *decreases* with *increasing* pressure. Further, reactivity *decreases* considerably with increasing CO partial pressure. The BYU coal char samples produced at high heating rates exhibited similar behavior; i.e., increasing reactivity with CO₂ partial pressure. The BYU chars were found to be much more reactive at high temperatures than the BU samples, but exhibited larger apparent activation energies, such that their reactivities became more comparable to that of the BU Wyodak samples at lower temperatures. This was attributed to the high heating rate ($\sim 10^5$ K/s) and very short pyrolysis times (~ 100 ms) experienced by the samples in the BYU FFB. This did not allow any time for thermal annealing, and thus produced high concentrations of active carbon sites.

This project also addressed the issue of fuel flexibility anticipated in next generation systems by providing a large database of comparative reactivities on coals and alternative solid fuels. A hybrid chemical/statistical model was developed that explains most of the observed reactivity variation based on four variables: the amounts of nano-dispersed K, nano-dispersed (Ca+Mg), elemental carbon (wt-% daf), and nano-dispersed vanadium, listed in decreasing order of importance. Catalytic effects play a very significant role in the oxidation of most practical solid fuel chars. Some degree of reactivity estimation is possible using only elemental analyses of parent fuels, but only if correlative techniques make use of the existing body of knowledge on the origin, form and dispersion of inorganic matter in various fuel classes.

Finally the project included a task in which advanced coal combustion submodels, Chemical Percolation and Devolatilization (CPD) and Carbon Burnout Kinetic (CBK) were modified and incorporated into a comprehensive computational CFD code. These models were implemented as subroutines in B&W's CFD code, COMOSM. In order to realize the increased accuracy from these advanced models the coal/char constituent model was reformulated to allow variable rates of progress for different gaseous products during devolatilization and char oxidation. This report gives a technical specification for the interface between these models and related chemical processes and physical properties.

Overall, the effects of elevated pressure, temperature, heating rate, and alternative fuel use are all complex and much more work could be further undertaken in this area. Nevertheless, the current project with its new data, correlations, and computer models provides a much improved basis for model-based design of next generation systems operating under these new conditions.